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THE SOIL FILTER: A TREATMENT PROCESS FOR REMOVAL OF ODOROUS GASES

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Final Report for the Federal Water Pollution Control
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16. Abstract
While the removal of odors emitted from various locations in sewage collectio systems by pumping the gases through a soil filter has been well documented, ~~Howev~~ the actual removal mechanisms remained to be established. The experiments performec volved variation of the average particle size and moisture content of the filters, and fu experiments were also performed with sterile soil. It was determined that the soil filte was particularly effective in the removal of polar gases such as hydrogen sulfide and me mercaptan from waste streams. At hydrogen sulfide concentrations in excess of 100 mg/ the biological removal mechanisms were not significantly operative, and chemical remov mechanisms appeared to prevail. In dry sterile soil, adsorption coupled with surface ca lysis reactions were found to be the predominant mechanisms for removal. For low gas concentrations (less than 100 mg/l H_2S) the biological removal mechanisms were predomi and wet soil was preferred. Moist loam soil was able to remove 100% of a 775 mg/l mercaptan, in quantities of .85 liter per cu. ft. of soil/week. Methane was not removed in any case. With proper design and care, soil filters operated in a range favorable for th growth of microorganisms can be operated indefinitely. (Lowry-Texas)

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THE SOIL FILTER: A TREATMENT PROCESS FOR REMOVAL OF ODOROUS GASES

Introduction

Since prehistoric times, man's industrial and domestic activities have been a source of water and air pollution. Until recently the odor aspect of the pollution problems has been generally neglected because it normally created only a nuisance problem. With the current trend of industrialization changing man's living patterns from rural to urban environments, many odor sources suddenly are adjacent to population centers. The rapid rate of industrialization and urbanization has created many new odor sources, and the concentration effects of cities has created intensification and dispersion problems for malodorous gases which heighten their effect on the surrounding environment.

Malodors from many industrial and domestic processes can create objectionable or unhealthful conditions in the area contiguous to the process. Liquid wastes in transit often are accompanied by malodorous volatile materials which emanate from sewer vents into the surrounding atmosphere. Many of these volatiles are perceptible in very low concentrations in the range of parts per billion. Disagreeable odors associated with the transportation of wastes are of serious concern to the responsible regulatory and control agencies and to citizens in the vicinity where the odors are discernible. These odor problems are intensified by warm summer temperatures, by long detention times in transit, by lack of aeration and by the close proximity of residences to sewer system vents.

Farm and animal production activities too can have problems of odorous gas productions. These odor problems are aggravated by current practices of large scale animal production and handling in confined areas. Mismanagement or negligence in the handling of animal wastes in these areas provides opportunities for increased and often almost intolerable odor concentrations.

Gas production from industry can be not only a serious problem to control but also a detriment to industry-community relationships. As an example of industrial odor problems, the kraft pulp mills are one of the largest emitters of methyl mercaptan with daily emissions capable of reaching as high as 2,500 pounds in a 100 ton pulp mill which practices no form of odor control (Kenline and Hales, 1963). In addition to the methyl mercaptan release, other obnoxious gases such as hydrogen sulfide, dimethyl sulfide and dimethyl disulfide are emitted from these same locations (Bethge and Ehrenborg, 1967). The majority of these emissions originate in the digester blow system and recovery furnace although smaller amounts escape from a variety of miscellaneous sources. Table I compares the threshold values of these common pulp mill malodors.

Table I

Some Common Malodorous Gases Emitted From Pulp Mills (Summer, 1963)

Gas	Formula	Threshold Odor (ppm by volume)
Methyl mercaptan	CH_3SH	11×10^{-4}
Hydrogen sulfide	H_2S	11×10^{-4}
Dimethyl sulfide	$(CH_3)_2S$	12×10^{-3}
Dimethyl disulfide	$(CH_3)_2S_2$	Not available

Thse pulp mill malodors can be compared to some of the common sewage gases shown in Table II. (Other gases include methane and the indoles.

Table II

Some Malodorous Gases Emitted From Sewers and Sewage Treatment Plants (Summer, 1963)

Gas	Formula	Threshold Odor (ppm by volume)
Methyl mercaptan	CH_3SH	11×10^{-4}
Hydrogen sulfide	H_2S	11×10^{-4}
Ethyl mercaptan	CH_3CH_2SH	18×10^{-7}
Skatole	C_9H_9N	75×10^{-9}

The degradation and removal of these objectionable gases in soil filters has been found to be an effective means of preventing the escape of these volatiles into the atmosphere. Results and methods for controlled laboratory testing of soil filters treating individual volatile gases are described below. The ability of the soil filter to provide adequate treatment marks this unit as an economical useful treatment process.

Production of Sewage Odors

The volatile materials responsible for objectionable sewage odors from domestic sewage result from the biological destruction of the organic solids in wastewater. These offensive gases can be created when organic material becomes deposited in the sewer or other appurtenances of the system, especially during periods of low flow and low velocity, or when, because of long detention periods of waste water without aeration, the oxygen content is depleted. The ensuing anaerobic conditions result in putrefaction of organic material and production of malodorous gases such as hydrogen sulfide or skatole.

Whether the cause of such anaerobic conditions are the result of poor design or natural features such as terrain, temperature or long distances between users and treatment facilities, conditions may prevail which make it extremely difficult to design or modify the treatment system to avoid the production of malodorous gases. The disposal of the undesirable gases must then be considered.

Putrefaction results in four categories of odorous products: (a) the inorganic gases including hydrogen sulfides and ammonia; (b) the acids such as acetic, lactic, and butyric; (c) the toxics - indole, skatole, phenols and mercaptans; and (d) the amines - cadaverine and putrescine (Harrow and Mazur, 1962; Cantarow and Shepartz, 1962).

Many of the most characteristic malodorous gases, such as hydrogen sulfide, produced by anaerobic decomposition contain sulfur. The possible organic sources of sulfur are the amino acids (cystine, methionine and lanthionine) as well as taurine, ethereal sulfates, sulfites, thiourea, alkaloids, the vitamins, thiamine and biotin, and the mercaptans (Harrow and Mazur, 1962; Starkey, 1950). Under anaerobic conditions, cystine would be the first amino acid to give off hydrogen sulfide (Waksman and Starkey, 1931; Porter, 1946). Activated sludge cultures using cystine as a substrate have gone anaerobic with production of hydrogen sulfide within 20 minutes during centrifugation (Carlson, 1965) a shorter time than with methionine.

Of the inorganic sulfur sources, sulfates would be the only major source in domestic wastewater. Sulfates in significant concentrations could be present also in ground-water infiltration. Other sources are free sulfur, polythionates, and thiocyanate. Industrial sources offer a variety of by-products and waste product sources of sulfur.

Hydrogen sulfide production rates in biological systems are most rapid at 30°C. Hence low flows with long detention times during the summer months are most apt to give rise to maximum odor problems.

The Soil Filter

Reference to the principle of deodorization of air streams by passage through beds of soil was first mentioned by Pomeroy (1959). Pomeroy claimed that passing air laden with sewage gases through a gas permeable soil bed, removed the malodorous gases as a direct consequence of their oxidation by biological growths. Promeroy based his hypothesis on both laboratory and field scale tests. In the laboratory, an air stream containing iso-valeric acid, skatole and phenol was passed through a column of moist clay soil, two inches in diameter by two feet in depth. No odor was detectable at the column exit but, according to Pomeroy, "Because of the exploratory nature of this test, no quantitative measurements were made."

The field scale tests were conducted at a sewage pump station in Long Beach, California using two identical soil diffusion trenches with a total gas flow of 730 cubic feet per minute. No odors were detected emerging after the odor of an overlying straw mat ceased but no data or mention was given concerning changes in soil biota.

The next recorded field scale studies used odors created in sewage pump station wet wells on Mercer Island, Washington (Mayo, 1962). Whereas Pomeroy's field studies were conducted by pumping sewer gases through the soil, in the Mercer Island installations the gases were forced out of the air tight wet well by the rising sewage level. When the sewage reached the level where pumps began operating, some of the gases previously expelled together with some air in the soil interstices were drawn back into the wet well. That is to say, a breathing action occurred which resulted in a longer soil residence time than if the gases were simply pumped through the bed. The soil filter consisted of four inch plastic distribution pipes covered by two inches of gravel and eighteen inches of soil, the ground surface area being a function of sewage flow through the wet well. Table III indicates the surface areas thought to be desirable for specified sewage flows.

Table III
Mercer Island Soil Filter Design Specifications

Flow in Sewer - gpm	Ground Level Surface Area sq. ft.	Perforated Distribution Pipe Length - Feet
Under 800	25	1 - 10 ft. pipe
800 - 1800	50	2 - 10 ft. pipe
1800 - 2500	100	4 - 10 ft. pipe

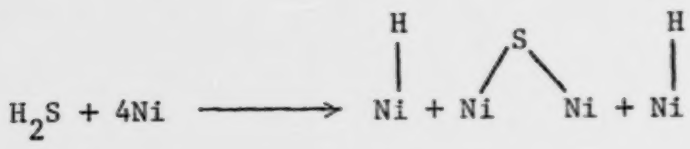
Work on soil filters at the University of Washington was first reported in 1964 (Carlson and Leiser, 1964). Those first experiments were concerned with biological aspects of removal in soil systems. Later work covered chemical removal considerations and ground flow aspects of gas movement in soils as well. Various laboratory setups were used including soil boxes and cylindrical columns of varying sizes. These laboratory studies concentrated on the removal of single gases especially hydrogen sulfide, methyl mercaptan and methane in varying concentrations and under different laboratory conditions. Flow, soil filter volume and area, moisture content, temperature, gas concentration, organism concentration, soil composition, and gas pressure were among the parameters considered in evaluating soil filter performance as a malodorous gas treatment unit.

CHEMICAL ASPECTS OF SOIL FILTER ACTIVITY

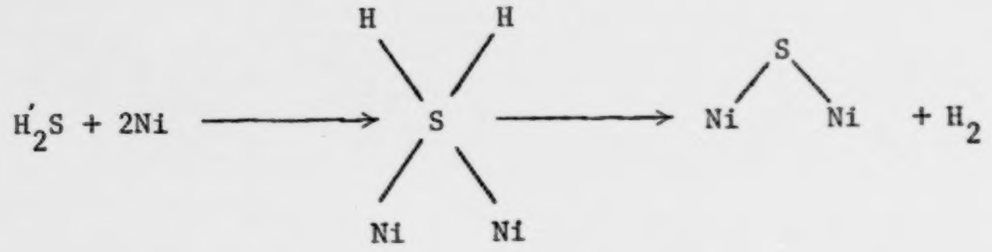
At high concentrations of hydrogen sulfide, in the range of hundreds of parts per million, rapid biological action does not appear to be the operative mechanism for removal of gas in the soil filter. The possibility then exists for chemical action as a means of removal. Chemical mechanistic alternatives include adsorption, water solution, ion exchange, and surface catalysis. A discussion of these mechanisms in terms of hydrogen sulfide as a typical malodor follows:

Adsorption

Chemical adsorption or chemisorption has been explored by Den Besten and Selwood (1962) in studies on the interaction between hydrogen sulfide gas and an artificially prepared nickel surface. The mechanisms of removal at low surface coverage were attributed to the formation of four bonds per hydrogen sulfide molecule chemisorbed. The hypothesized reaction was pictured as:



At high surface coverage, the dissociated hydrogen atoms appeared to be forced from the nickel surface to the gas phase by the more strongly attracted sulfide atoms:



Approximately two thirds of the hydrogen atoms initially entering in the hydrogen sulfide molecule were eventually removed as molecular hydrogen by degassing the nickel surface at high temperatures. The other one-third was thought to be trapped between the nickel surface and the sulfide layer.

A similar dissociative chemisorption was noted by Roberts and Ross (1966) with interactions between hydrogen sulfide and an artificially prepared iron surface. In this case the authors did mention a stoichiometric relationship. The suggested reaction was:

$$xFe(s) + H_2S(g) \longrightarrow Fe_xS(s) + H_2(g)$$

Thus in both cases hydrogen gas was a product.

Siedlewski (1966) studied the adsorption interaction between activated carbon and hydrogen sulfide. The oxides of carbon were found to be "active centers" responsible for the chemisorptive removal. These centers were not blocked by hydrogen sulfide adsorption evidently because the activated carbon acts as a catalyst in the oxidation of hydrogen sulfide to sulfur, the sulfur then migrating away from these active centers making them available for further catalytic action.

Water Solution

Solution of hydrogen sulfide gas in water present in the soil interstices and in the water film covering the soil surface may be hypothesized as being involved in gas removal via the soil filter. The minimum solubility of hydrogen sulfide in distilled water may be calculated using Henry's Law .

$$\bar{p} = Hx$$

where $\bar{p}$ = partial pressure of hydrogen sulfide in the gas phase-atmospheres

H = partial pressure of hydrogen sulfide in the gas phase in equilibrium with the solution-atmospheres/mole fraction

x = mole fraction of hydrogen sulfide soluble in the water under equilibrium conditions.

For Henry's Law to be valid, no ensuing chemical reaction with the solvent should occur. At partial pressures less than one atmosphere the calculations normally should be correct within a few percent.

Table IV indicates the solubility of hydrogen sulfide at pH 7 for various water temperatures and hydrogen sulfide partial pressures (Gumerman, 1968). A sample calculation appears in the appendix (Foust, 1960).

Ion Exchange

Soil fractions less than 20 microns in diameter (i.e. clay, silt and organic fractions) are generally thought to be responsible for ion exchange reactions (Bear, 1964). Three types of anion reactions are possible.

1. The replacement of counter-ions which are held by the soil as the result of unequal force distribution within the crystal. Such sites for exchange may occur at broken surfaces, plane surfaces, and within the crystal structure itself. The unequal force distribution at these sites is attributed to the influence of low pH upon hydroxyl groups occurring in clays and hydrous oxides of iron and aluminum. For example, under acid conditions, a typical hydroxyl group from an inorganic crystal structure could behave as follows:

$$\text{R-OH} + H^+ + Cl^- \rightleftharpoons \text{R-Cl} + H_2O$$

TABLE IV : CALCULATED MINIMUM SOLUBILITY OF HYDROGEN SULFIDE IN DISTILLED WATER

Milliliters of hydrogen sulfide which will dissolve in 100 grams of water at a gas pressure of 760 mm.

Temperature of H_2O - °C	Gas Phase Concentration of Hydrogen Sulfide - ppm						
	1	10	100	1000	10^4	10^5	Pure
0	4.65×10^{-4}	4.65×10^{-3}	4.65×10^{-2}	0.465	4.65	46.5	465
10	3.40×10^{-4}	3.40×10^{-3}	3.40×10^{-2}	0.340	3.40	34.0	340
20	2.58×10^{-4}	2.58×10^{-3}	2.58×10^{-2}	0.258	2.58	25.8	258
30	2.05×10^{-4}	2.05×10^{-3}	2.05×10^{-2}	0.205	2.05	20.5	205
40	1.67×10^{-4}	1.67×10^{-3}	1.67×10^{-2}	0.167	1.67	16.7	167
50	1.41×10^{-4}	1.41×10^{-3}	1.41×10^{-2}	0.141	1.41	14.1	141
60	1.21×10^{-4}	1.21×10^{-3}	1.21×10^{-2}	0.121	1.21	12.1	121
70	1.05×10^{-4}	1.05×10^{-3}	1.05×10^{-2}	0.105	1.05	10.5	105
80	9.22×10^{-5}	9.22×10^{-4}	9.22×10^{-3}	0.0922	0.922	9.22	92.2
90	8.65×10^{-5}	8.65×10^{-4}	8.65×10^{-3}	0.0865	0.865	8.65	86.5

with the chloride ion now acting as a counter-ion.

$$R\text{-}Cl + NO_3^- \rightleftharpoons R\text{-}NO_3 + Cl^-$$

The major factors determining the importance of this mechanism of anion exchange are the accessibility of hydroxyl groups, the geometry of the replacing anion, and the valence of the replacing anion (Grim 1953).

2. Exchange of lattice ions is another prevalent mechanism. Such isomorphic replacement normally occurs at broken clay edges, but not on surfaces. A typical exchange of this type occurs in the isomorphic displacement of hydroxyl ions from clays and hydrous oxides by fluorine ions. This may be pictured in the following way:

$$R\text{-}OH + F^- \rightleftharpoons R\text{-}F + OH^-$$

As in the previous mechanism, size and valence of the replacing anion are critical factors (Bear, 1964).

3. Although probably not of significance in this research, certain tetrahedral anions, such as phosphate, borate and arsenate, may extend the lattice by adsorption to the edges of silica tetrahedron s. Note that these three anions are all of similar size to the silica tetrahedron. In terms of our definition of ion exchange, reactions of this type might be better classified as adsorptions.

Only in cases where a liquid film exists upon the soil particles could ion exchange be an anticipated hydrogen sulfide removal mechanism. Exchange mechanism two appears to be the only one of the three which could take place in this research. Mechanism one requires acidic conditions, such conditions favoring the hydrogen sulfide to remain primarily in the unionized aqueous form. Mechanism three requires a tetrahedral shape, which only sulfate possesses, and which H_2S, HS^-, and $S^=$ do not possess.

Contact Catalysis

Grant (1960) has investigated the interaction between hydrogen sulfide and three types of activated carbon; 1) Pittsburgh Chemical Company type BPL, 2) type BPL impregnated with copper, and 3) type BPL impregnated with both copper and iron. Results indicate that both the copper and copper-iron impregnated carbons yield removal superior to the non-impregnated type BPL carbon, the copper-iron carbon being the more efficient of the two impregnated carbons studies. The principal purpose of the study was the determination of the hydrogen sulfide removal mechanism and the most efficient regeneration method for the spent carbon. Regeneration methods studied included steam purging, degassing, air purging, and various combinations of these three at varying temperatures and moisture conditions. The most effective regeneration technique was air purging at 100°C in the presence of a slight amount of water vapor; air purging at temperatures greater than 100°C yielded no increase in regeneration efficiency, but regeneration at room temperature appeared to be only partially effective.

During passage of hydrogen sulfide over the copper impregnated carbon, the carbon changed color from black to blue; while the iron-copper impregnated carbon changed from red to black upon contact with hydrogen sulfide. These color changes were felt by Grant (1960) to indicate the formation of blue cupric sulfide from black cupric oxide, and of black iron sulfide from red ferric oxide. Upon regeneration with room temperature air, the original color of the carbon returned, except that yellow deposits were noted on the carbon surface. These deposits were identified as amorphous sulfur.

Several removal mechanisms were postulated to account for the increased removal capacity of the impregnated carbons over the unimpregnated type BPL carbon, which removed the hydrogen sulfide by physical adsorption. Grant (1960) suggested that the equations defining the removal process were:

$$CuO + H_2S \longrightarrow CuS + H_2O$$

$$Fe_2O_3 + 3H_2S \longrightarrow 2FeS + S + 3H_2O$$

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

In addition, the following equations defining the regeneration by air oxidation were hypothesized:

$$CuS + 1/2O_2 \longrightarrow CuO + S$$

$$2FeS + 3/2O_2 \longrightarrow Fe_2O_3 + 2S$$

$$Fe_2S_3 + 3/2O_2 \longrightarrow Fe_2O_3 + 3S$$

One specific problem of hydrogen sulfide removal pertains to the removal of hydrogen sulfide from natural gas, prior to its delivery to the customer. Although the hydrogen sulfide may be removed by "wet" chemical processes, the most common method used is the passage of the gas over a solid adsorbent, usually iron oxide or zinc oxide (Nonhebel, 1964).

Griffith and Morcom (1945) studied the interaction between hydrogen sulfide mixed with natural gas and seven forms of ferric oxide, αFe_2O_3, $\alpha Fe_2O_3 \cdot H_2O$, $\beta Fe_2O_3 \cdot H_2O$, ∂Fe_2O_3, $\partial Fe_2O_3 \cdot H_2O$, $\delta Fe_2O_3 \cdot H_2O$ and amorphous Fe_2O_3. Identification of the various ferric oxide forms was determined by the rate of change of their magnetic properties on heating and their rate of solution in a standard acid solution. All forms, except the β form were said to react with hydrogen sulfide to yield a hydrated ferric sulfide, as shown below:

$$2Fe_2O_3 \cdot H_2O + 6H_2S \longrightarrow 2Fe_2S_3 \cdot H_2O + 6H_2O$$

$$2Fe_2O_3 + 6H_2S \longrightarrow 2Fe_2S_3 \cdot H_2O + 6H_2O$$

Their results also indicated that the hydrated ferric sulfide may be readily oxidized back to ferric oxide when the temperature is less than 50°C and the pH greater than seven. Under dry conditions, the authors found that the $Fe_2S_3 \cdot H_2O$ is oxidized to $\alpha Fe_2O_3 \cdot H_2O$, but under moist conditions, the oxidation product is $\partial Fe_2O_3 \cdot H_2O$. At temperatures greater than 50°C, dehydration of the $Fe_2S_3 \cdot H_2O$ occurred, and the resulting anhydrous sulfide oxidized very slowly. In addition, the Fe_2S_3 produced by dehydration was found to decompose, yielding FeS_2 and Fe_8S_9. When these latter two forms were oxidized, they yielded respectively, ferric sulfate and a completely inactive ferric oxide.

Not all of the oxide forms studied by Griffith and Morcom (1945) showed identical removal capabilities. The $\alpha Fe_2O_3 \cdot H_2O$ and $\partial Fe_2O_3 \cdot H_2O$ gave the best removals, the $\alpha Fe_2O_3 \cdot H_2O$ being slightly superior. An interesting situation occurred when some of the less active oxides were reduced to the sulfide form, and then oxidized in a dry environment, thus being converted to the very active $\alpha Fe_2O_3 \cdot H_2O$ form. Because $\alpha Fe_2O_3 \cdot H_2O$ possessed the best removal capability, a relatively inactive form was converted to the most active form observed by a sulfiding-oxidation cycle.

Summary

For the removal of H_2S by dry, sterile soil, adsorption and surface catalysis appear to be the mechanisms which could be operative. Due to the relatively large surface areas presented by soil, adsorption appears to be a likely prospect. However, the large percentage of metals in soil suggests that surface catalysis reactions may also be prevelant.

Naturally, it is logical to expect some hydrogen sulfide removal by water solution in wet soils. No information is available to determine the rate of solution. Once solution of hydrogen sulfide takes place, the exchange of one of its ionized forms with lattice ions in the soil appears to be possible. Therefore, removal by moist soils depends upon the rate of hydrogen sulfide solution in water.

Chemical Removal Studies

The ability of soils to remove sulfides from solution was studied by batch and dynamic testing. The batch uptake tests were run on a dry and wet basis in stoppered 500 ml erlenmeyer flasks and 300 ml BOD incubation bottles respectively. Dynamic uptake tests were run in 2-1/4 diameter plastic columns 8-1/2 inches tall. Analytical methods are described in the appendix. Unaltered sterile soils and prepared cation sterile soils were investigated for their ability to remove sulfide from solution. The majority of the tests were run at pH 5.8, the natural pH of Lynden loam used as the test soil.

Liquid-Soil Batch Uptake Tests

Using the apparatus and technique described, the ability of unaltered sterile soils and prepared cation saturated sterile soils to remove sulfide from solution was investigated. The majority of this testing was conducted at pH 5.8, since this was the natural pH of Lynden loam. Although the addition of sodium sulfide tended to slightly increase the pH of the buffered solution, the buffer possessed sufficient strength to maintain the solution pH to within 0.2 pH units of that desired at all times. In spot checks using a much more concentrated buffer solution, no pH change was observed, but identical removals were obtained.

The passing two-hundred sieve fraction of sterile Lynden loam was used to determine the influence of solution pH upon soil removal ability. As shown by Figure 2, the best removal occurred at pH 8.0, lesser removal occurring at lower pH values. The strong dependence of removal upon temperature at pH values of 5.8 and 8.0 may be seen in Figure 3. Note that Figure 3 illustrates the equilibrium position, and in no way is intended to illustrate a rate effect.

Using sterile Lynden loam soil, the influence of sieve size upon removal at equilibrium is illustrated in Figure 4. In this figure, it can be seen that the best removal per gram of soil was produced by the smallest grain size fraction (largest sieve number), indicating that possibly soil surface area influences removal ability, assuming constant soil composition.

The influence of equilibrium removal ability of the passing two-hundred fraction of sterile Lynden loam when saturated with various common cations appears in Figures 5 and 6. The "washed" soil underwent four washings with distilled water, but otherwise no changes were made in the cation status.

The relationship between equilibrium removal capacity of the passing two-hundred fraction of sterile Lynden loam and a typical clay, sand, and humic soil (all sterile) may be observed in Figure 7. Elemental chemical analyses of the soils studied may be found in Tables V and VI.

Isotherms for data collected for sterile Lynden loam are presented according to the Freundlich and Langmuir isotherm models in Figures 8 and 9 respectively.

Gas-Soil Batch Uptake Tests

The capacity of dry soils to remove hydrogen sulfide from the gas phase was investigated using the previously described equipment. The

Table V : SUMMARY OF SOIL PROPERTIES IN LIQUID-SOIL SYSTEMS

Soil Property	Lynden loam P200	Humus P200	Lynden loam P140 - R200	Lynden loam P60 - R140	Sand P200	Clay P200
mg.Sulfide removed / gram of soil at an equil.conc. of 15 mg.l	16.2	15.4	10.4	7.8	7.3	4.0
%Fe	7.471	1.142	7.551	5.90	7.65	11.704
%Cu	0.0058	0.056	0.0044	0.0041	0.0053	0.0434
%Zn	0.0055	0.0154	0.0055	0.0055	0.0064	0.0130
%Pb	Trace	Trace	Trace	Trace	Trace	Trace
%Mn	0.0562	0.104	0.0613	0.0591	0.0641	0.0883
%Mg	0.827	0.072	0.928	0.938	1.019	2.349
%Ca	1.44	0.566	1.579	2.079	1.898	2.503
%Na	1.13	0.1789	1.48	1.62	1.57	2.503
%K	0.654	0.223	0.619	0.704	0.694	1.44
%Al	8.04	1.21	8.09	7.30	7.10	9.52
Σ elements analyzed - %	18.33	3.57	20.32	18.61	20.10	29.34
% Si, O, H, C, and trace	65.17	16.04	70.63	73.89	72.11	67.19
soil surface area (m^2/gram)	31.8	84.4	15.15	12.4	14.6	32.2
maximum EDTA uptake at pH 5.8 (mg/gram)	108	54.6	81.9	74.4	79.5	105.6
EDTA uptake / surface area (mg/m^2)	3.4	0.64	5.4	6.0	5.45	3.28
% volatile	16.5	80.4	9.35	7.5	7.79	3.57

Note: All percentage values are weight %.

Table VI: SUMMARY OF SOIL PROPERTIES IN GAS-SOIL SYSTEMS

Soil Property	Clay P200	Lynden Loam P200	Lynden loam P140 - R200	Humus P200	Lynden loam P60 - R140
equil. uptake capacity at 5550 ppm mg/gram of soil	181	18.3	12.1	11.3	9.2
%Fe	11.704	7.471	7.551	1.142	5.90
%Cu	0.0434	0.0058	0.0044	0.056	0.0041
%Zn	0.0130	0.0055	0.0055	0.0154	0.0055
%Pb	Trace	Trace	Trace	Trace	Trace
%Mn	0.0883	0.0562	0.0613	0.104	0.591
%Mg	2.349	0.827	0.928	0.072	0.938
%Ca	2.503	1.44	1.579	0.566	2.079
%Na	1.68	1.13	1.48	0.1789	1.62
%K	1.44	0.654	0.619	0.223	0.704
%Al	9.52	8.04	8.09	1.21	7.30
Σ elements analyzed - %	29.34	18.33	20.10	3.57	18.61
% Si, O, H, C, and trace	67.19	65.17	70.63	16.04	73.89
% volatile matter	3.57	16.5	9.35	80.4	7.5
soil surface area (m^2/gram)	32.2	31.8	15.15	84.4	12.4
maximum EDT uptake at pH 5.8 (mg/gram)	105.6	108	81.9	54.6	74.4
%Fe x surface area	377	236.5	114	96.4	73.2
$\frac{\text{\%Fe x surface area}}{\text{equil. uptake capacity at 500 ppm}}$	2.08	12.9	9.45	8.51	7.95

Note: All percentage values are weight %.

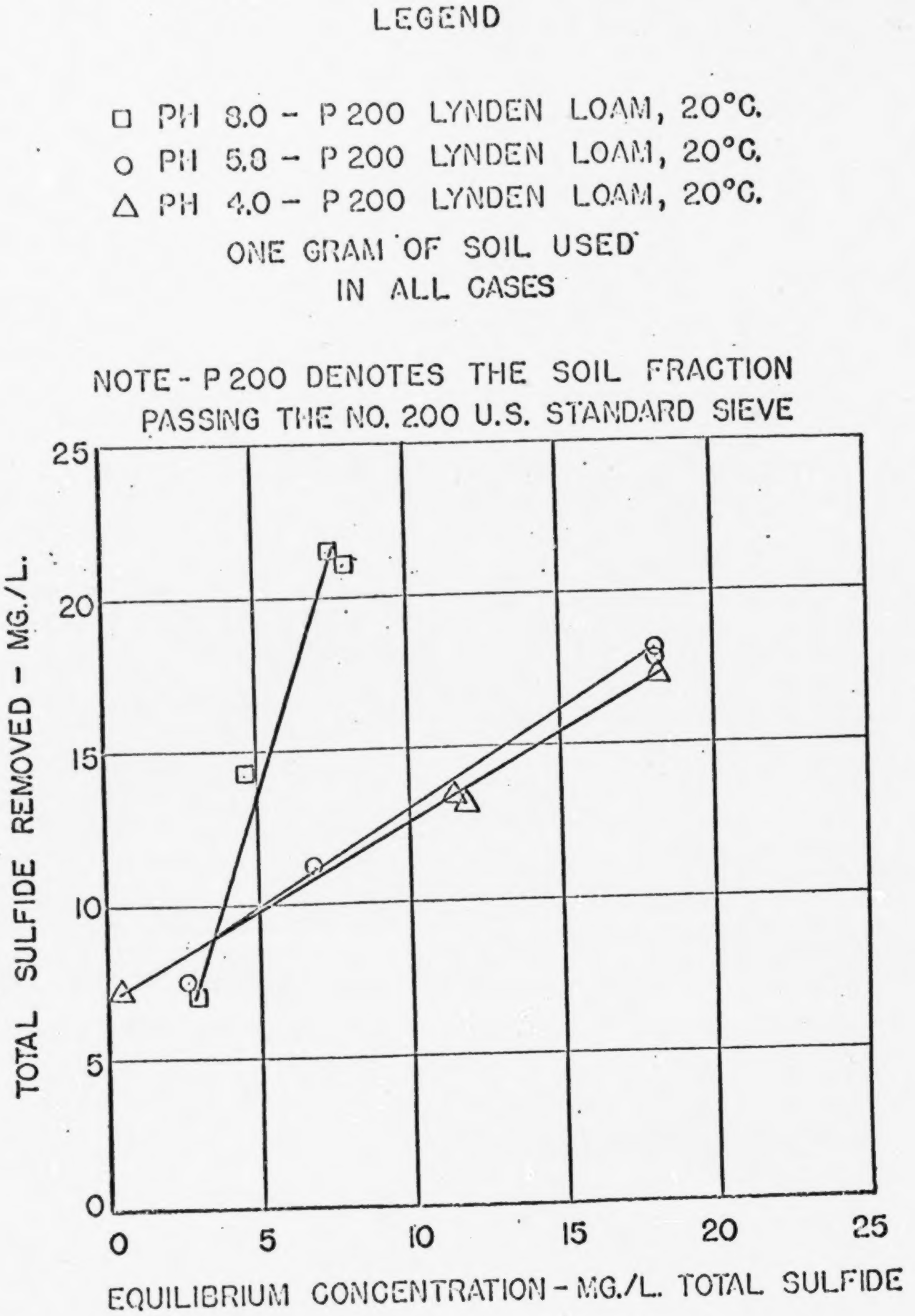


FIGURE 2 - PH INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

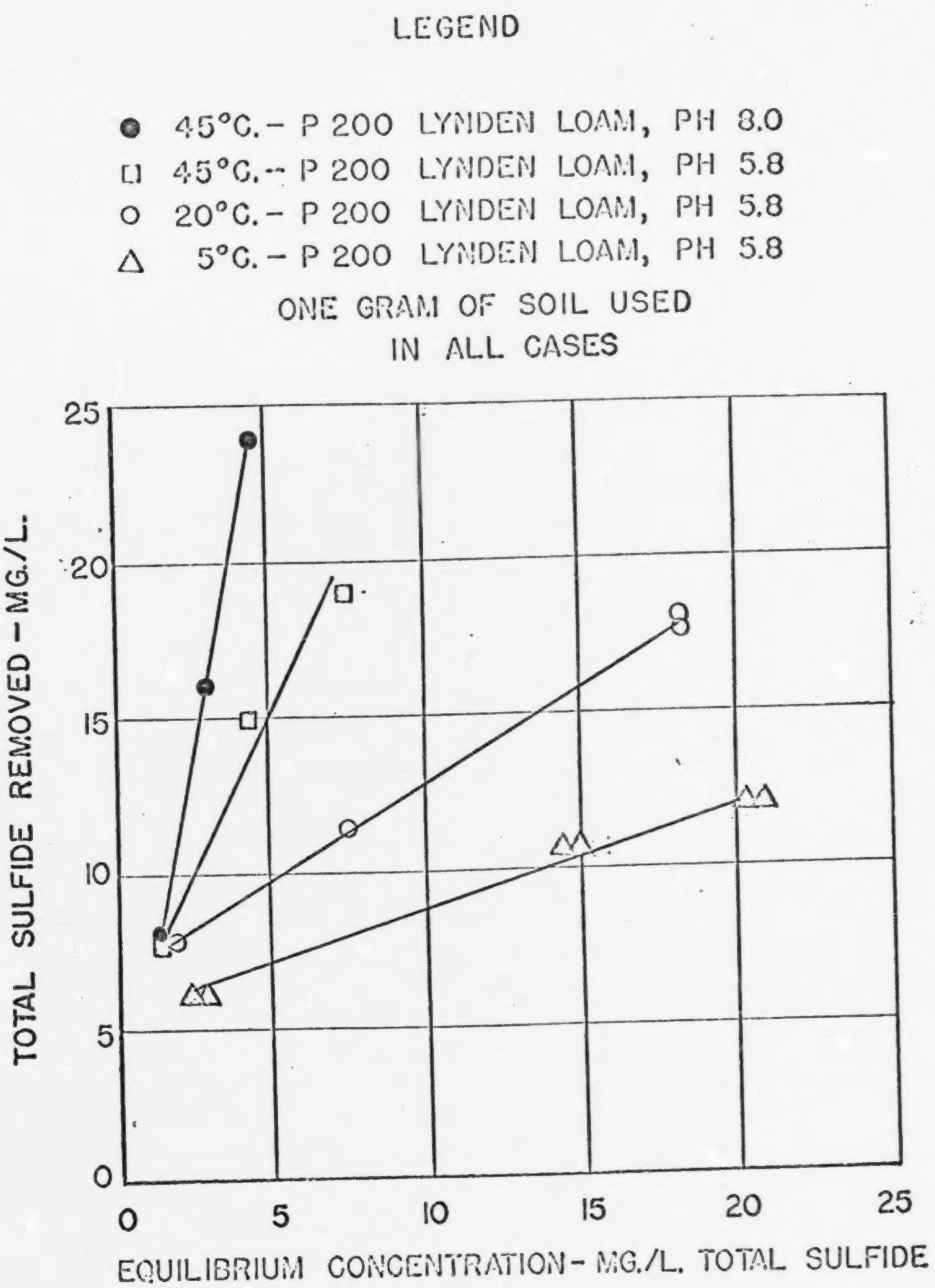


FIGURE 3 - TEMPERATURE INFLUENCE ON SULFIDE UPTAKE IN LIQUID - SOIL SYSTEMS

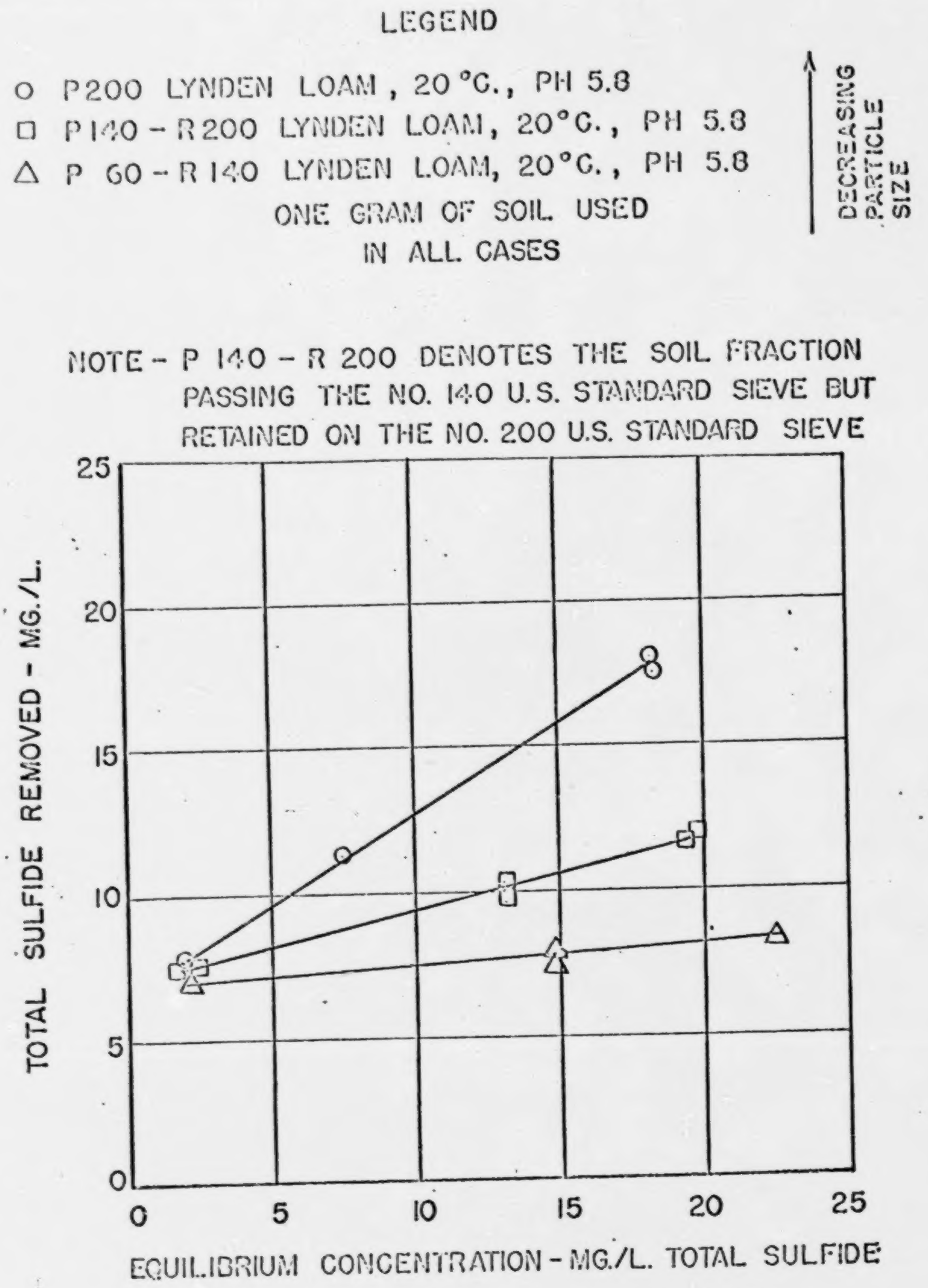


FIGURE 4 - SIEVE SIZE INFLUENCE ON SULFIDE UPTAKE IN LIQUID - SOIL SYSTEMS

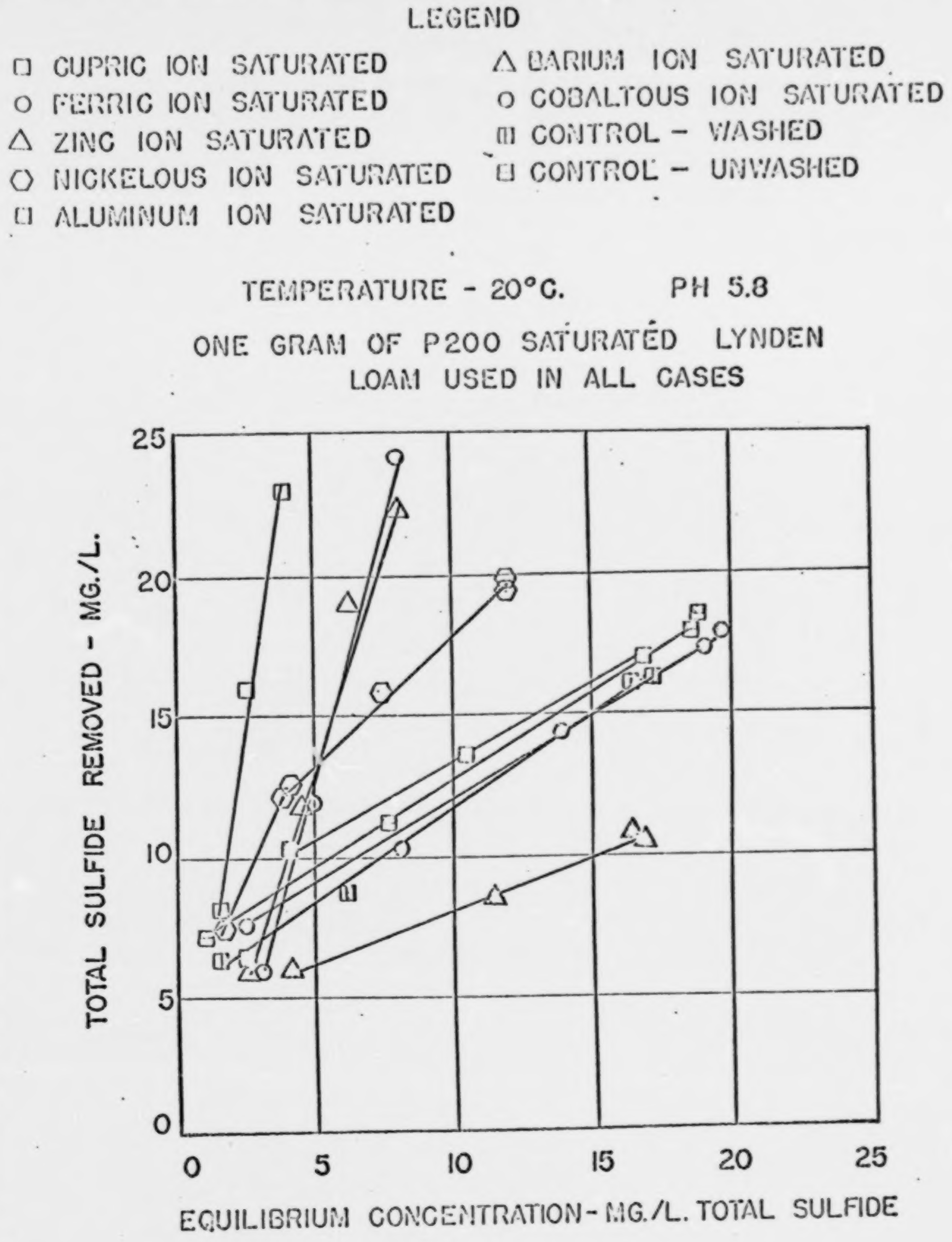


FIGURE 5 - CATION INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

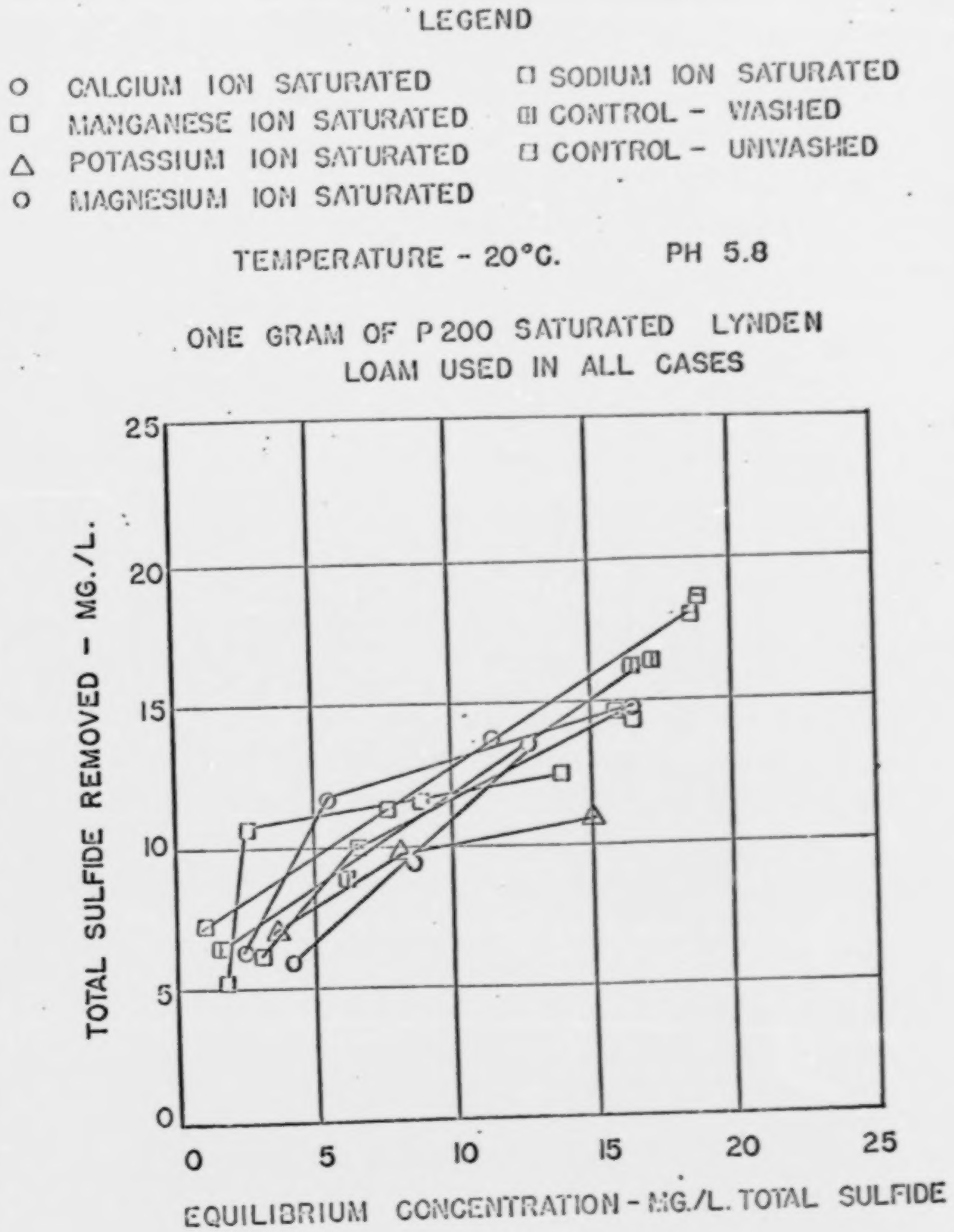


FIGURE 6 - CATION INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

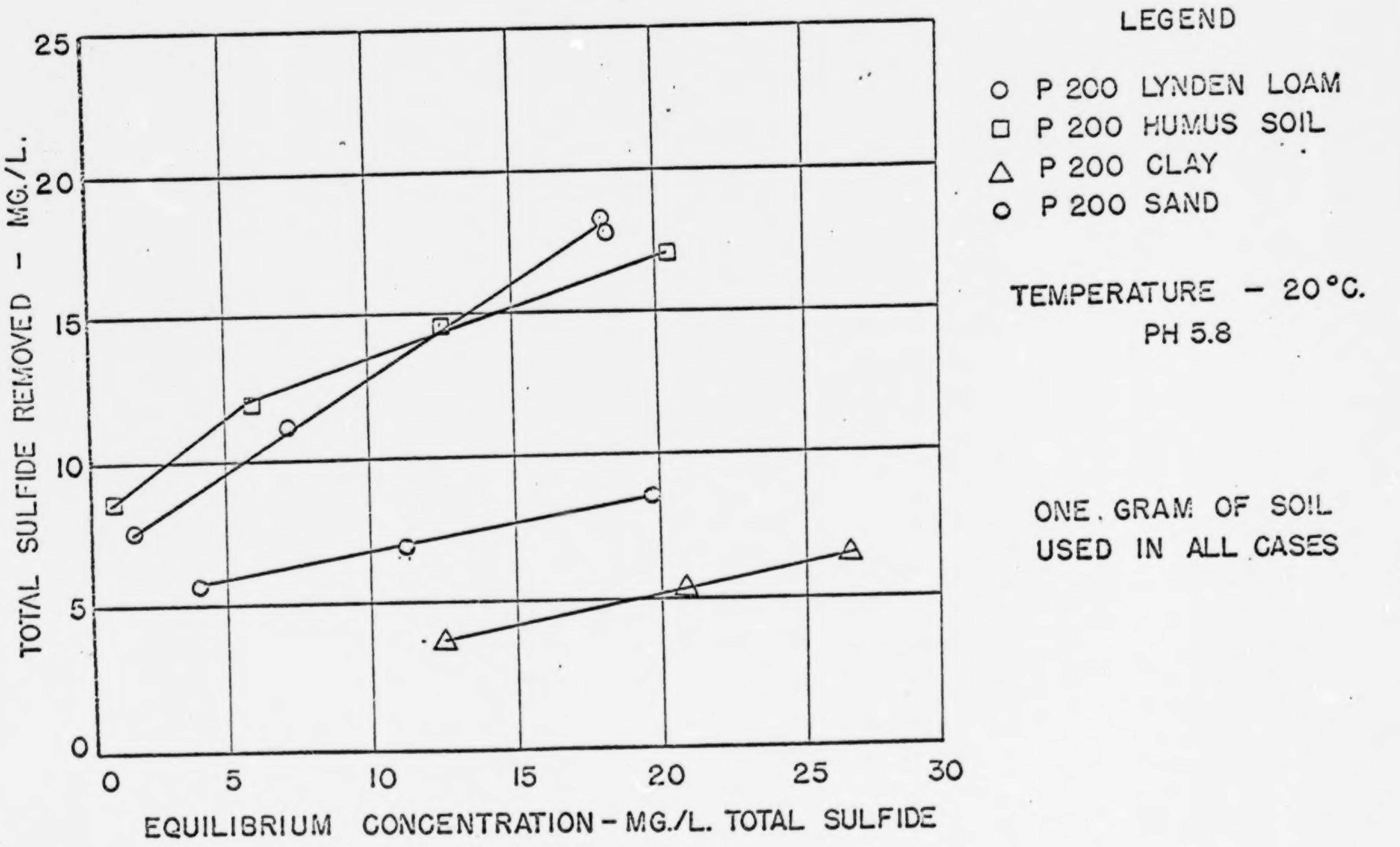


FIGURE 7 - SULFIDE UPTAKE BY SEVERAL SOILS IN LIQUID-SOIL SYSTEMS

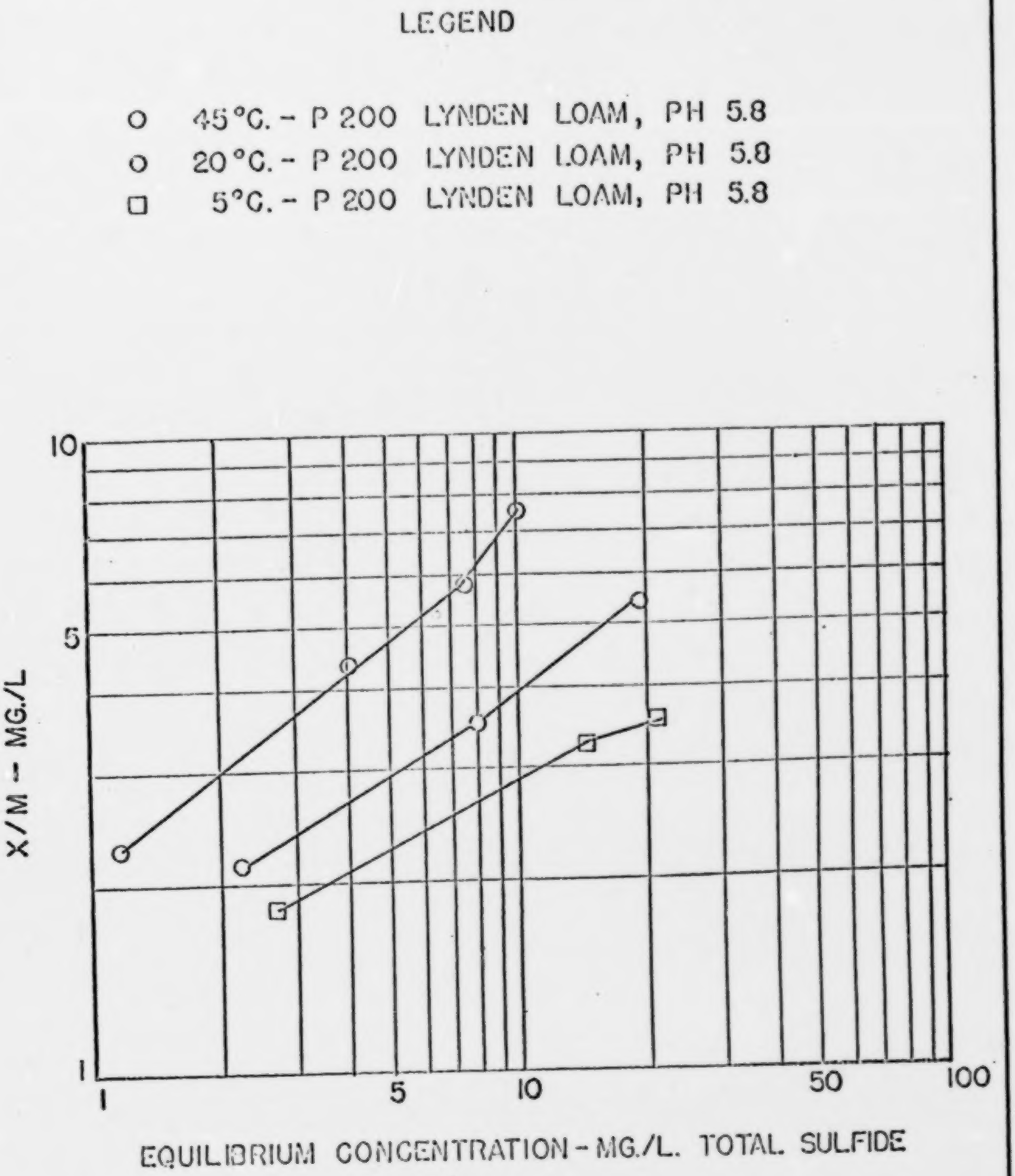


FIGURE 8 - FREUNDLICH ISOTHERM PLOTS FOR LIQUID - SOIL SYSTEMS

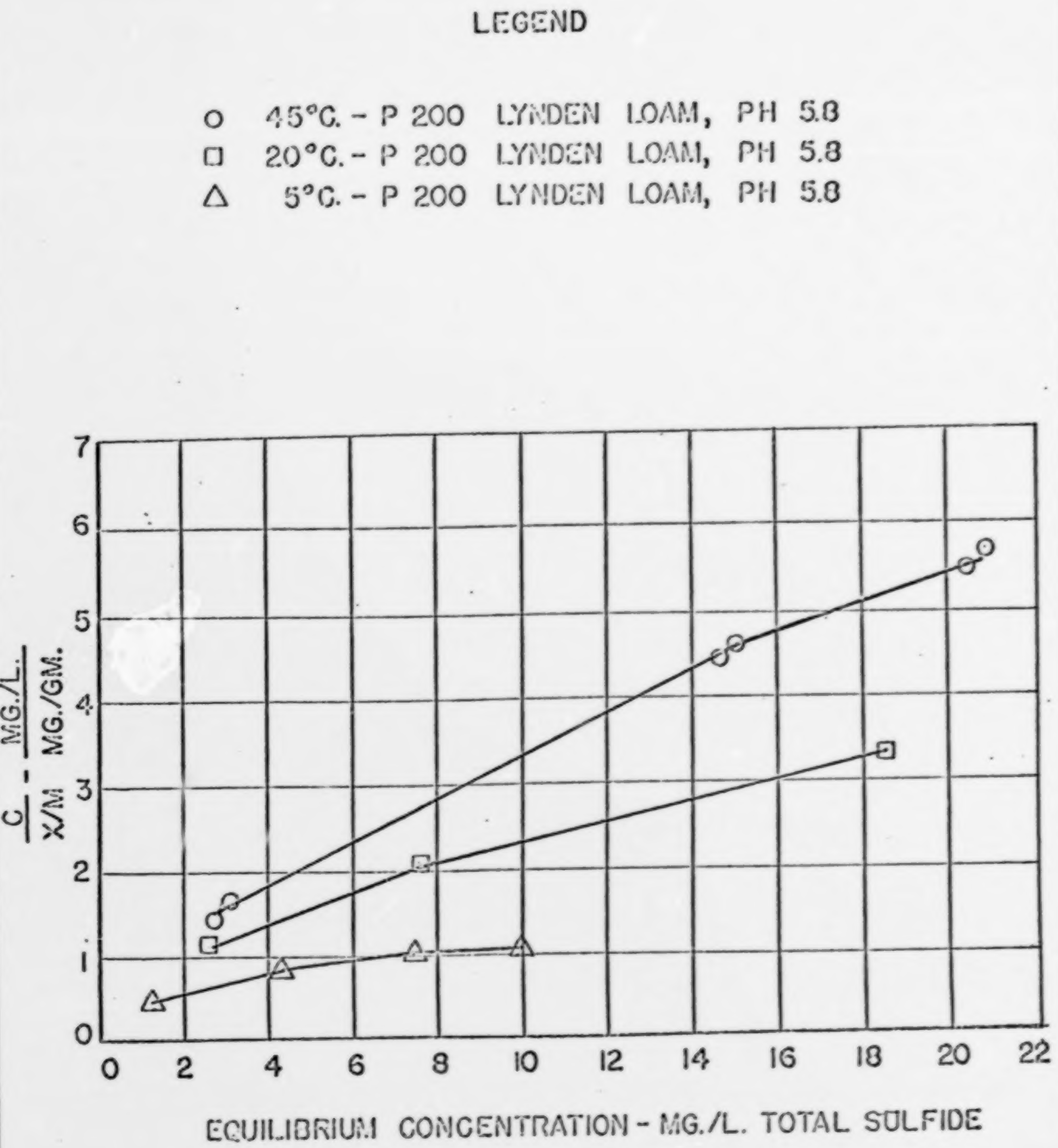


FIGURE 9 - LANGMUIR ISOTHERM PLOTS FOR LIQUID - SOIL SYSTEMS

temperature influence upon removal by the passing number 200 sieve fraction of sterile Lynden loam appears in Figure 10. Figures 12 and 13 show respectively Freundlich and Langmuir isotherm plots for various sieve fractions of sterile Lynden loam. Two larger size fractions of Lynden loam were also studied, the comparison between the uptake isotherms of these sterile fractions and the passing no. 200 sieve fraction may be seen in Figure 11. The influence of cation saturation upon the uptake isotherm of the passing no. 200 sieve fraction of sterile Lynden loam was also investigated. Results from these tests are shown in Figures 14 and 15. In these tests, the "washed" sample underwent four successive washings with distilled water, but the cation balance was unaltered in any other way. The uptake curve for unwashed P200 Lynden loam is also shown in Figures 14 and 15.

In addition to Lynden loam, a humic, a clay, and a sand soil (all sterile) were also studied to determine their ability to remove hydrogen sulfide from the gas phase. An uptake isotherm of the passing no. 200 sieve fraction for each of these sterile soils and also for Lynden loam appears in Figure 16.

Surface Area Measurements

The surface areas of all soil fractions in relation to liquid-soil and gas-soil uptake isotherms were measured using the modified ethelyene glycol monoethyl ether (EGME). Results of these measurements are shown in Table VII.

TABLE VII: SOIL SURFACE AREAS

Soil	Surface Area - $\frac{\text{square meters}}{\text{gram of soil}}$
P60-R140 Lynden loam	12.40
P140-P200 Lynden loam	15.15
P200 Lynden loam	31.8
P200 Sand	14.6
P200 Clay	32.2
P200 Humus	84.4

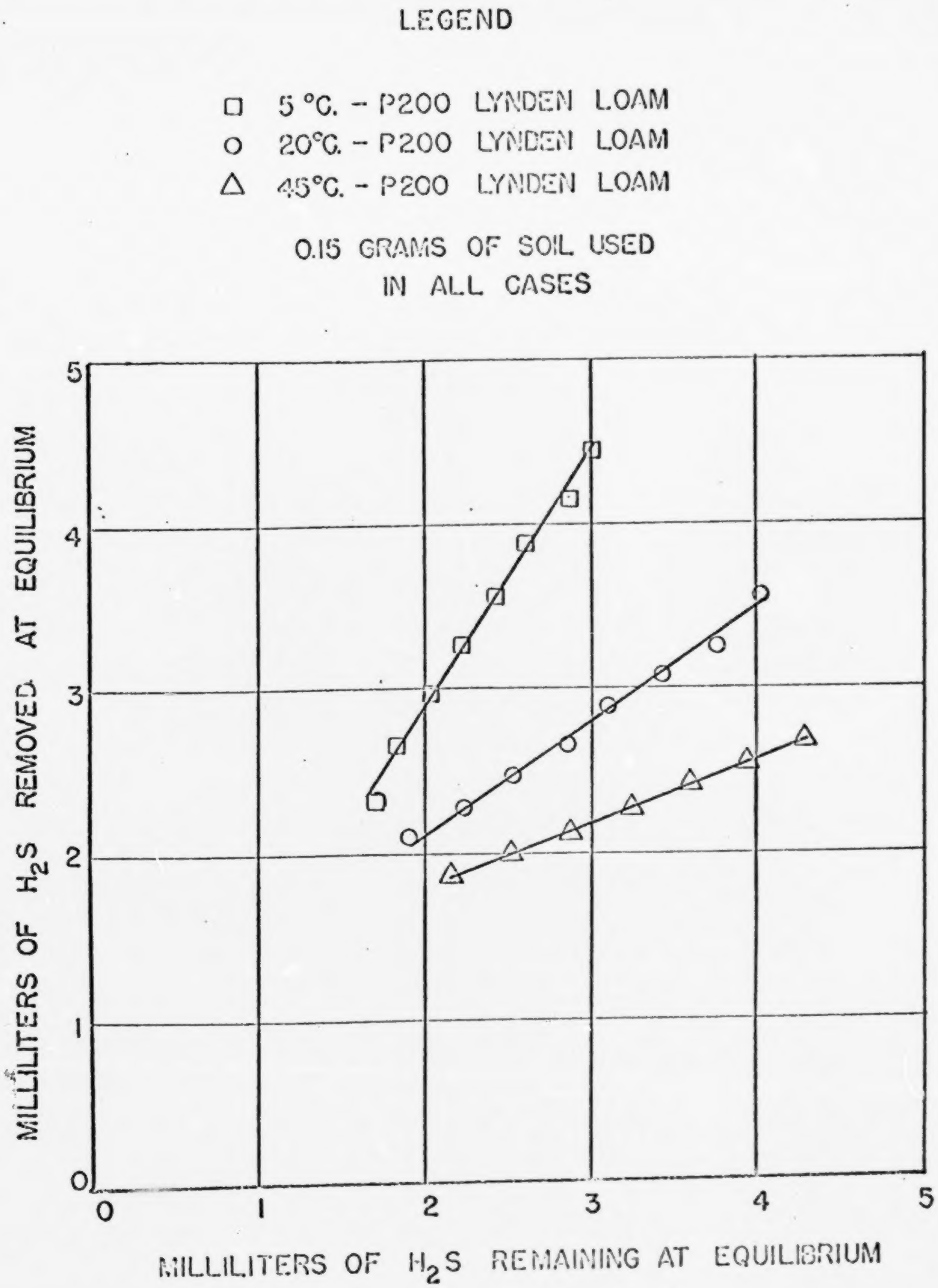


FIGURE 10 -- TEMPERATURE INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS - SOIL SYSTEMS

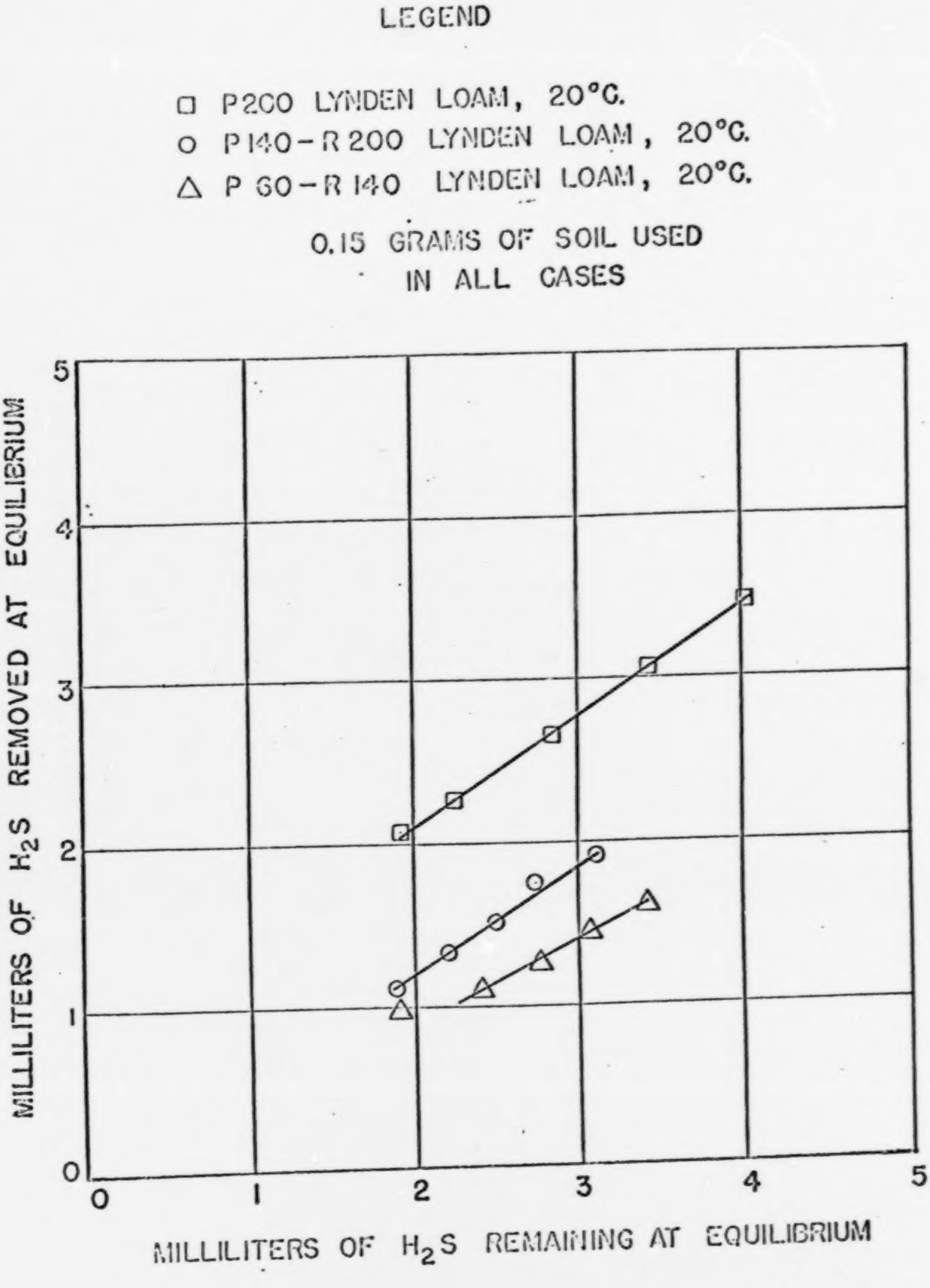
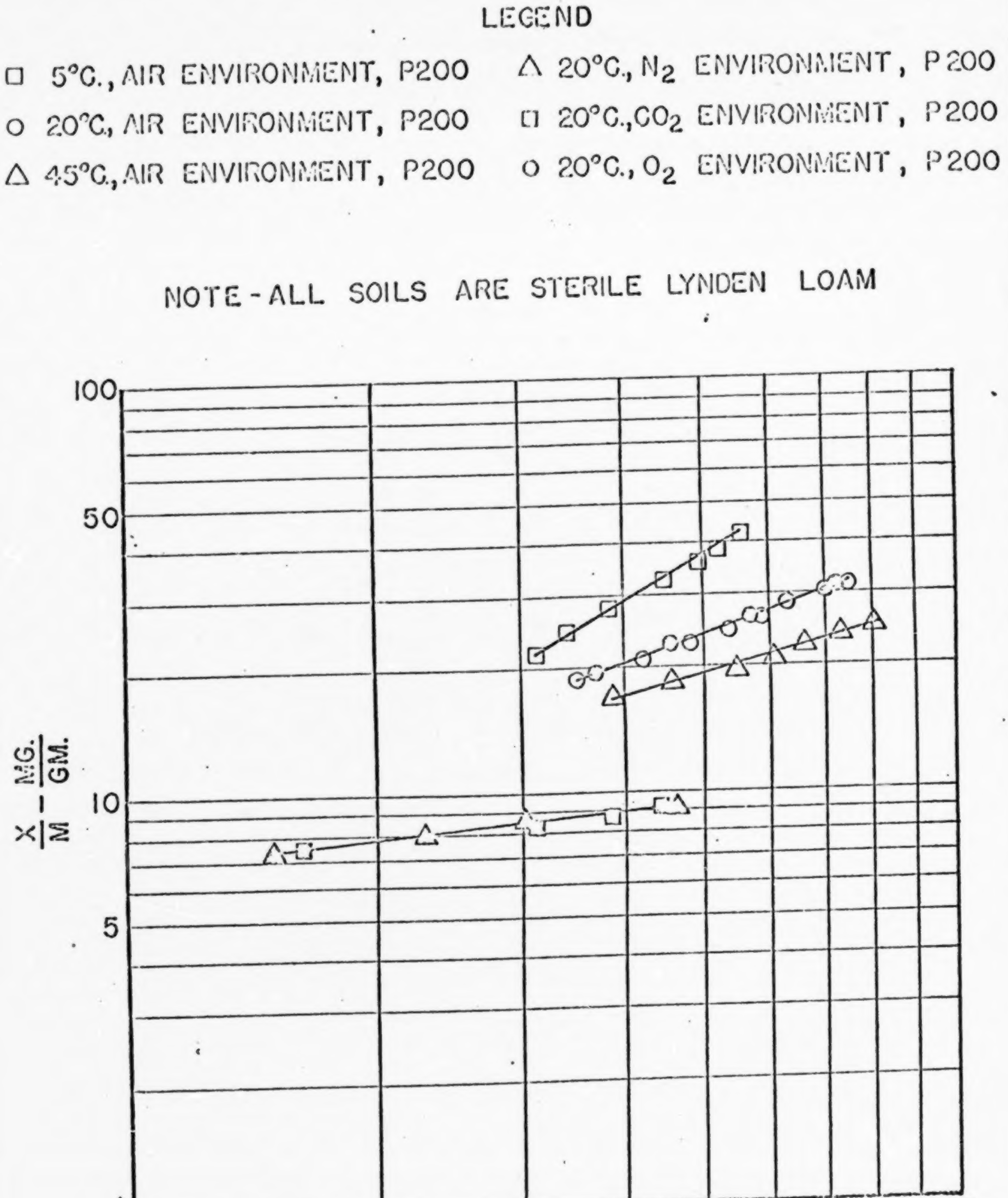


FIGURE II - SIEVE SIZE INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS



NOTE - ALL SOILS ARE STERILE LYNDEN LOAM

FIGURE 12 - FREUNDLICH ISOTHERM PLOTS OF GAS - SOIL SYSTEMS

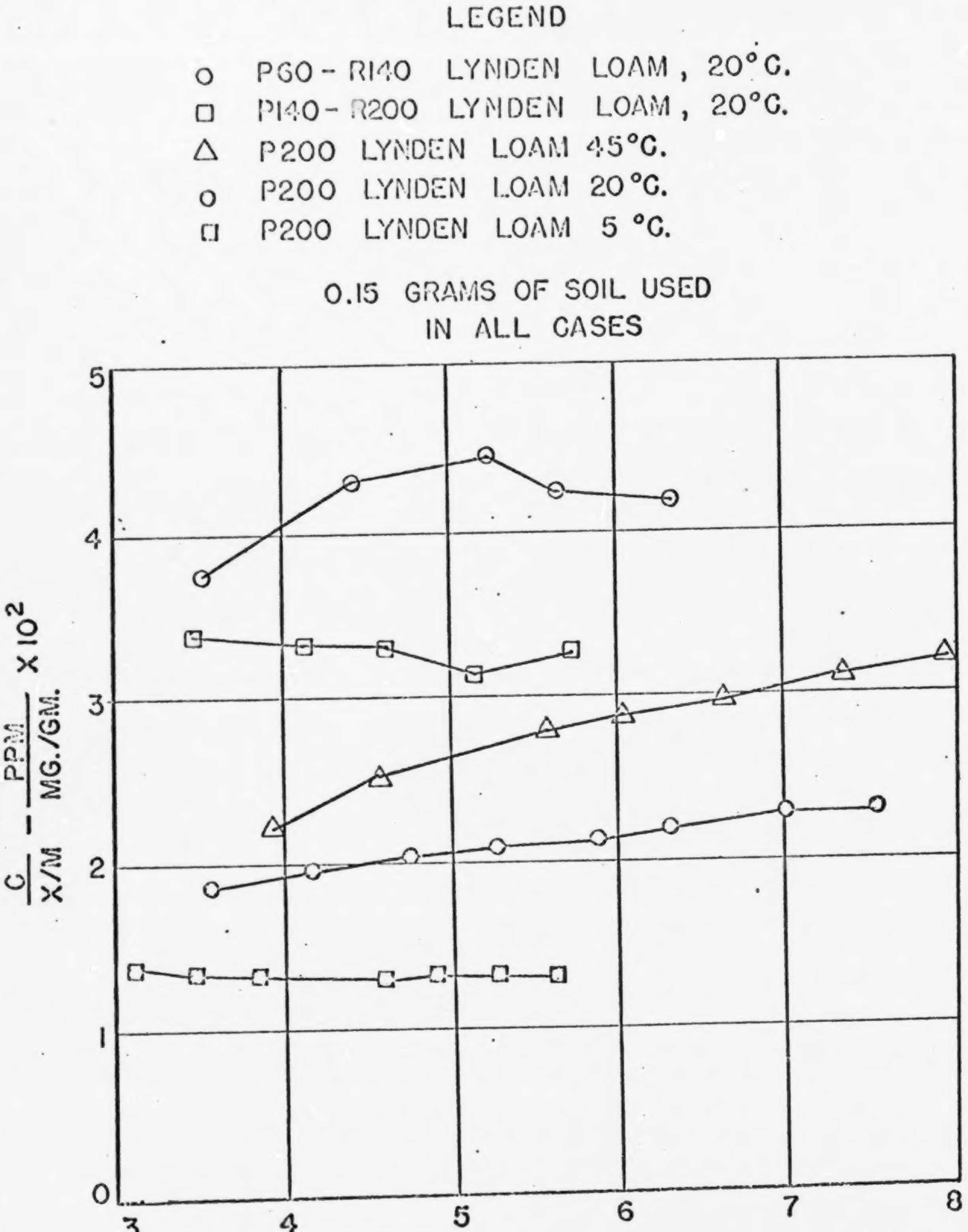


FIGURE 13 - LANGMUIR ISOTHERM PLOTS FOR GAS - SOIL SYSTEMS

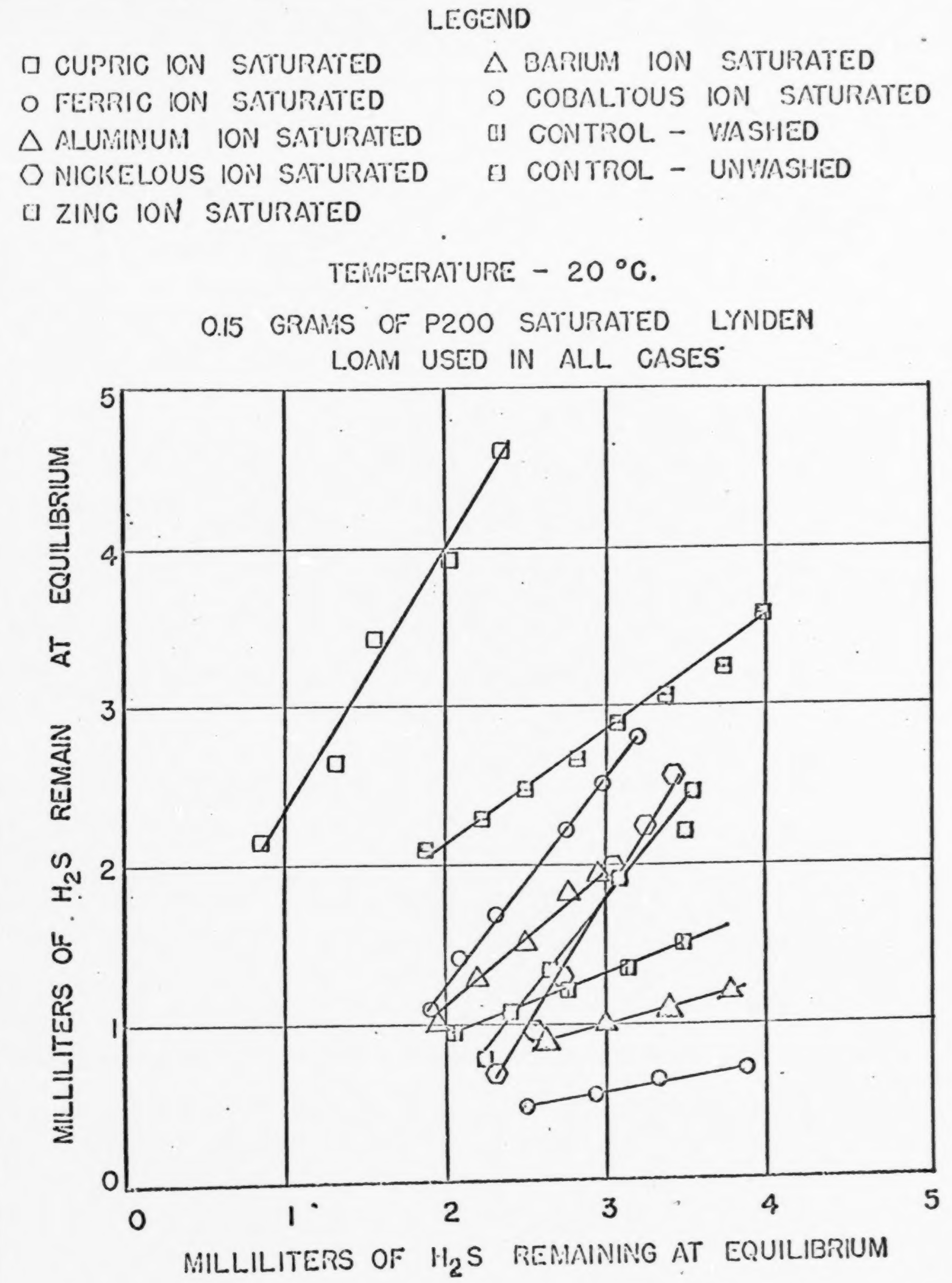


FIGURE 14 - CATION INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS

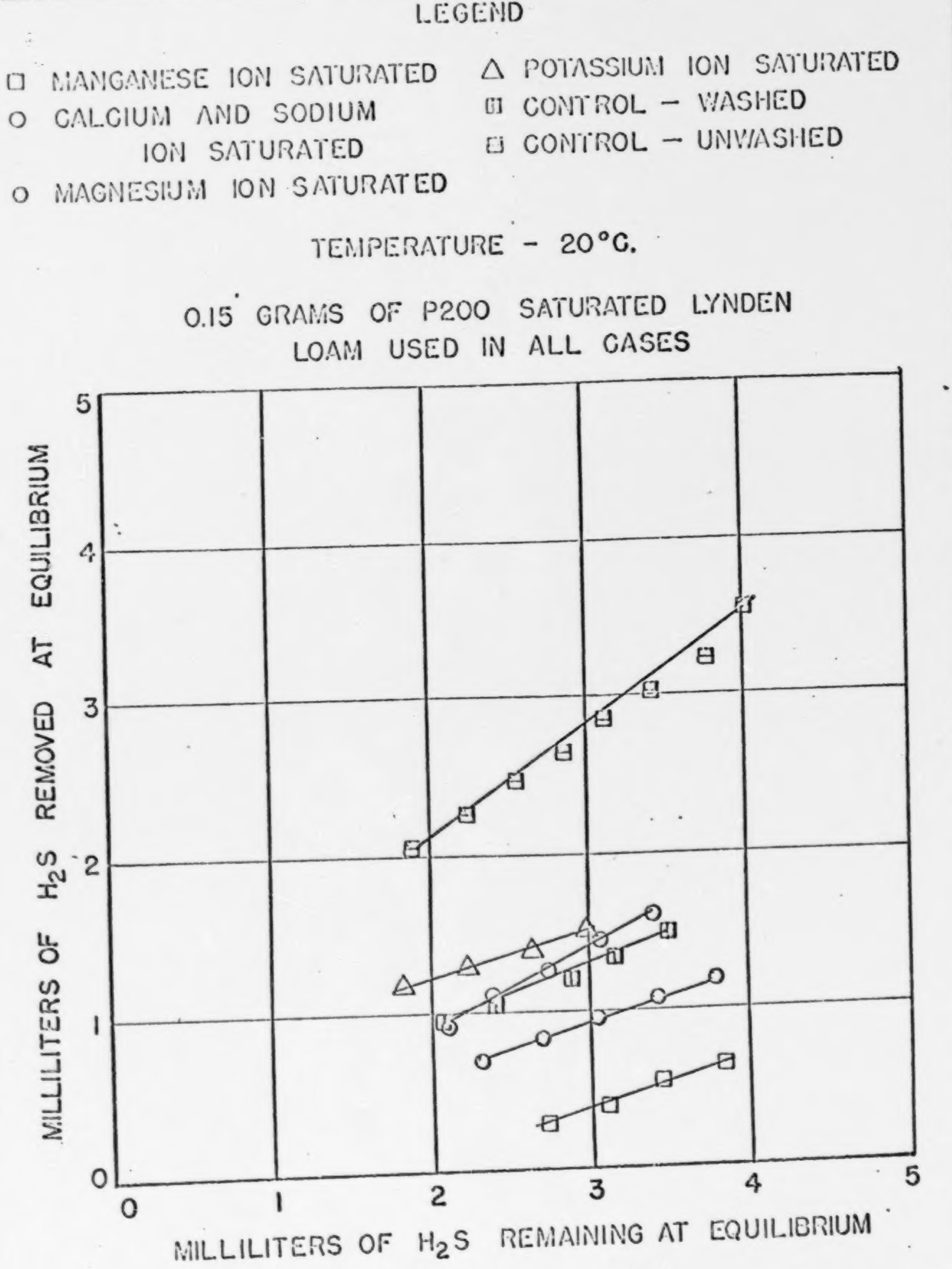


FIGURE 15 - CATION INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS

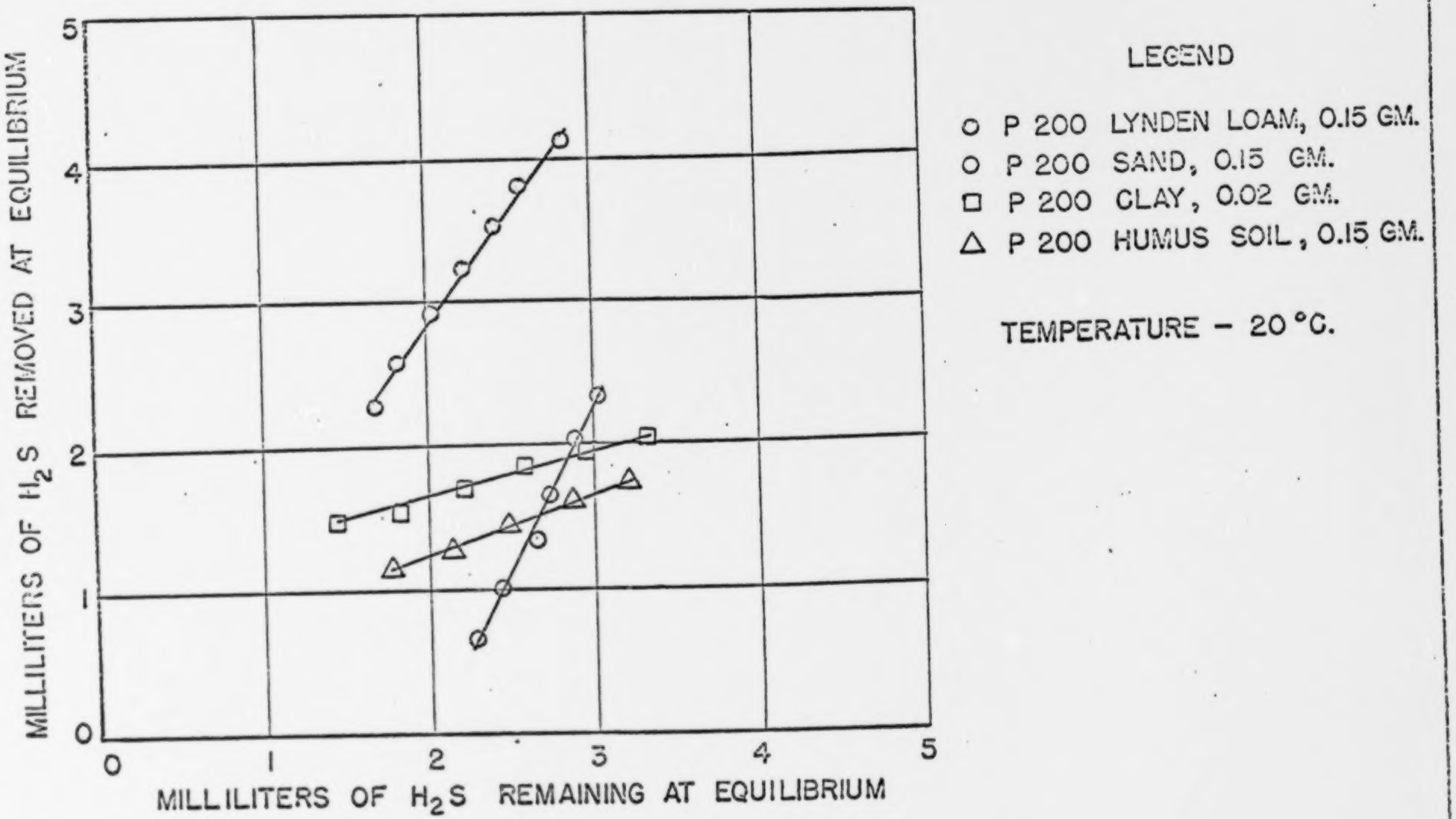


FIGURE 16 - HYDROGEN SULFIDE REMOVAL ISOTHERMS FOR SEVERAL SOILS IN GAS-SOIL SYSTEMS

EDTA Removal From Solution

The ability of sterile soil to remove ethylenediaminetetracetic acid (EDTA) from a buffered liquid solution was investigated as previously described. The maximum uptake of EDTA at pH 5.8 by the soils previously used in liquid-soil and gas-soil uptake experiments is shown in Table VIII.

TABLE VIII: EDTA UPTAKE BY VARIOUS SOILS

Soil	EDTA Uptake at Equilibrium - $\frac{\text{milligrams}}{\text{gram of soil}}$
P60-R140 Lynden loam	74.4
P140-R200 Lynden loam	81.9
P200 Lynden loam	108.0
P200 Sand	79.5
P200 Clay	105.6
P200 Humus	54.6

Dynamic Uptake of Hydrogen Sulfide from Air Streams

Using the plastic columns described previously, the ability of the passing number 10 sieve fraction of sterile Lynden loam to remove hydrogen sulfide from moving air streams was investigated. Figure 17 depicts the hydrogen sulfide breakthrough time for dry, sterile soil samples as the total flow rate increased and the hydrogen sulfide flow rate remained constant. Note that concentration decreases from left to right. The upper curve illustrates the results obtained using air as the carrier gas, while the middle curve shows the results with nitrogen used as the carrier vehicle. The lower curve represents calculated values of hydrogen sulfide breakthrough time, assuming no interaction occurring between the gas stream and the soil, and also that "plug-flow" exists at all times. Appearing in Appendix C are the calculations for this curve. In Figure 18, iso-concentration lines are shown on a plot of initial hydrogen sulfide breakthrough time versus total flow rate for previously unused dry, sterile soil samples.

The foregoing two figures represented only the time until initial breakthrough, the soil being disposed of after initial breakthrough. This work was complemented by a series of experiments undertaken to determine what effect the number of rejuvenations had upon hydrogen sulfide breakthrough time. These results are shown in Figure 19 as a plot of hydrogen sulfide breakthrough time versus the number of rejuvenations.

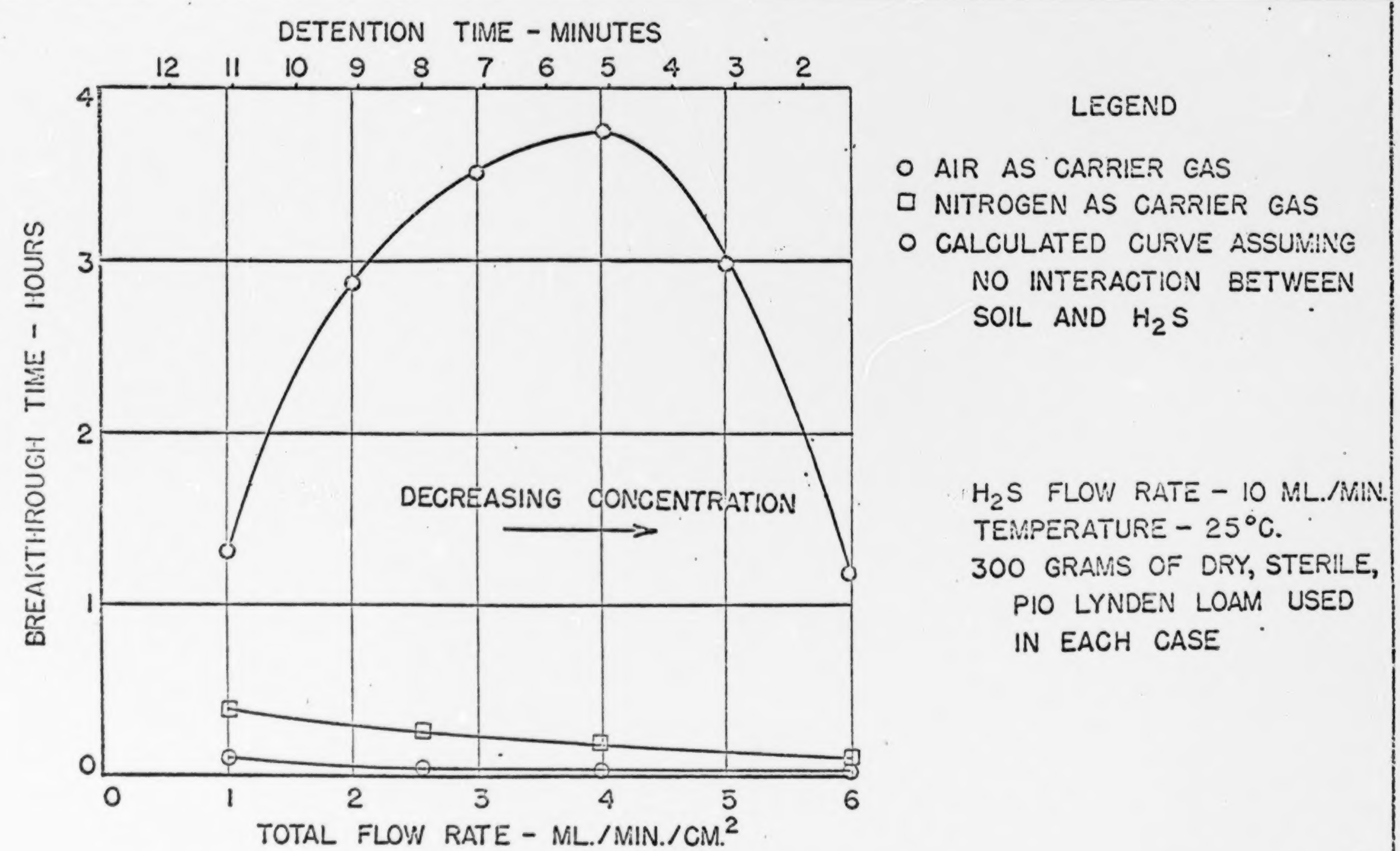
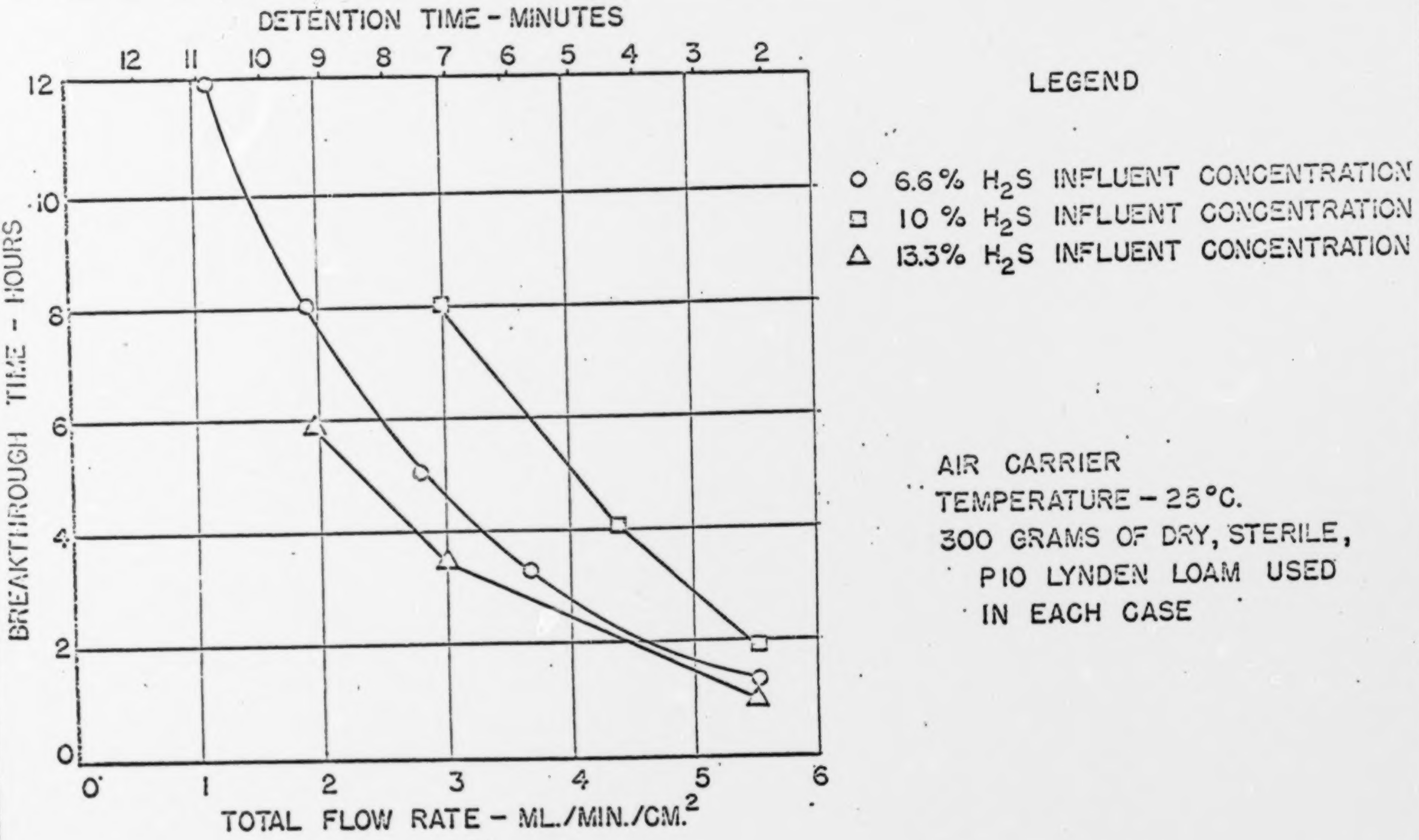
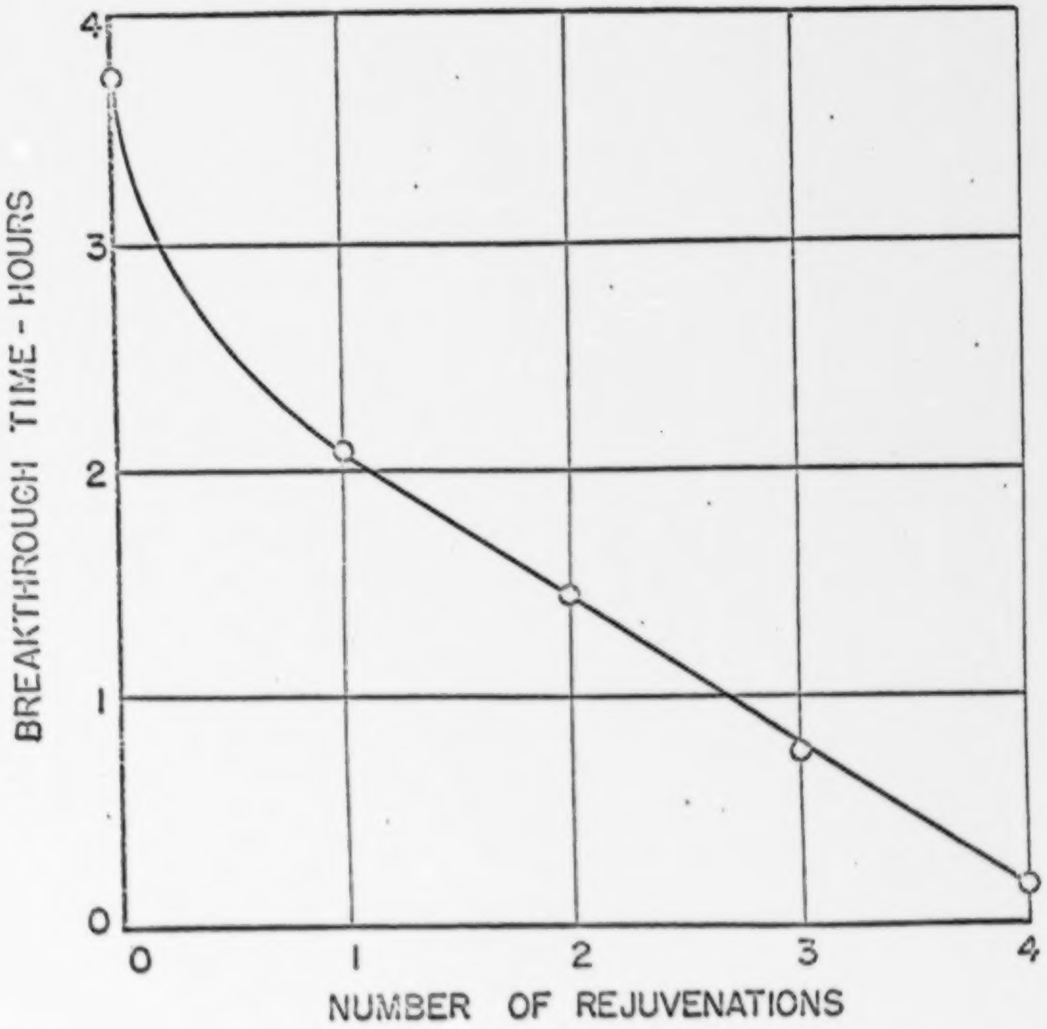


FIGURE 17 - H_2S BREAKTHROUGH TIME VERSUS TOTAL FLOW AT A CONSTANT H_2S FLOW RATE



AIR CARRIER
TEMPERATURE - 25°C.
300 GRAMS OF DRY, STERILE,
P10 LYNDEN LOAM USED
IN EACH CASE

FIGURE 18 - H_2S BREAKTHROUGH TIME VERSUS TOTAL FLOW AT FIXED H_2S CONCENTRATIONS



TOTAL FLOW - 3.91 ML./MIN/CM.^{2}
H_2S FLOW - 10 ML./MIN.
DETENTION TIME - 2.92 MIN.
TEMPERATURE - 25 °C.
300 GRAMS OF DRY, STERILE,
P10 LYNDEN LOAM USED
IN EACH CASE

FIGURE 19 - H_2S BREAKTHROUGH TIME VERSUS. NUMBER OF REJUVENATIONS

In Figure 20, the influence of influent gas temperature upon initial hydrogen sulfide breakthrough time may be observed. In addition to the previous experiments using dry soils, the influence of soil moisture content upon hydrogen sulfide breakthrough time was also investigated. These results may be seen in Figure 21.

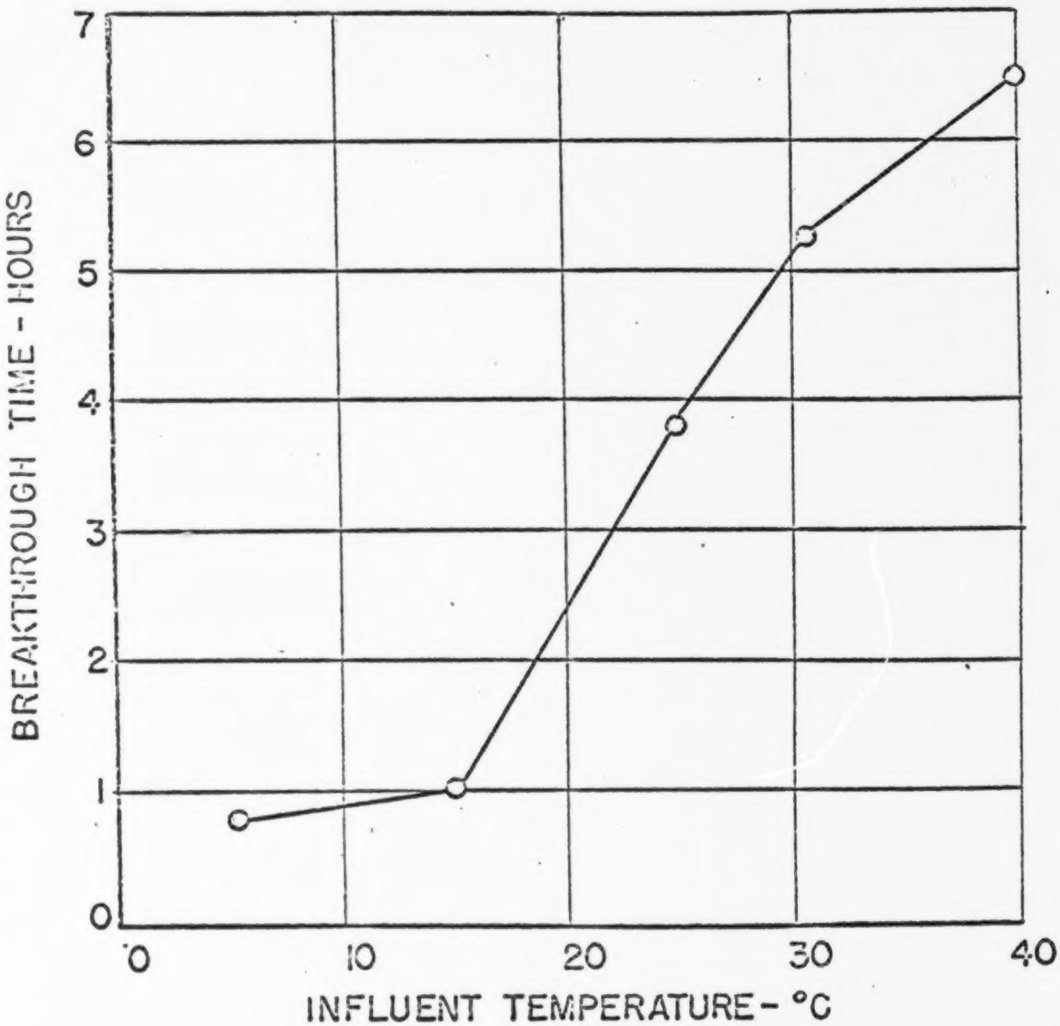
Influence of Moisture Upon the Removal Mechanism in Batch Scale Testing

Batch scale experimentation has been conducted using both wet and dry soils. In referring to this testing, systems using wet, sterile soil were denoted as liquid soil systems and those using dry, sterile soil as gas-soil systems. It should be noted that different sulfide species were present in the liquid-soil and gas-soil systems. As shown in Figure 22, aqueous hydrogen sulfide, hydrosulfide ion, or sulfide ion may be the predominant species in liquid-soil systems, the predominant species depending on the solution pH. In gas-soil systems, hydrogen sulfide gas was the only sulfide species present.

Changes in temperature produced opposite effects upon the equilibrium removal capacity in liquid-soil and gas-soil systems. At pH 5.8 liquid-soil systems, increasing temperatures exerted an increase in the equilibrium removal capacity as shown in Figure 3. Therefore, the sulfide removal mechanism in liquid-soil systems is endothermic. Conversely, as shown by Figure 10, gas-soil systems removed less hydrogen sulfide at equilibrium as temperatures increased. Gas-soil removal systems are therefore exothermic. On the basis of these observed results, different sulfide removal mechanisms are evident in wet and dry soil.

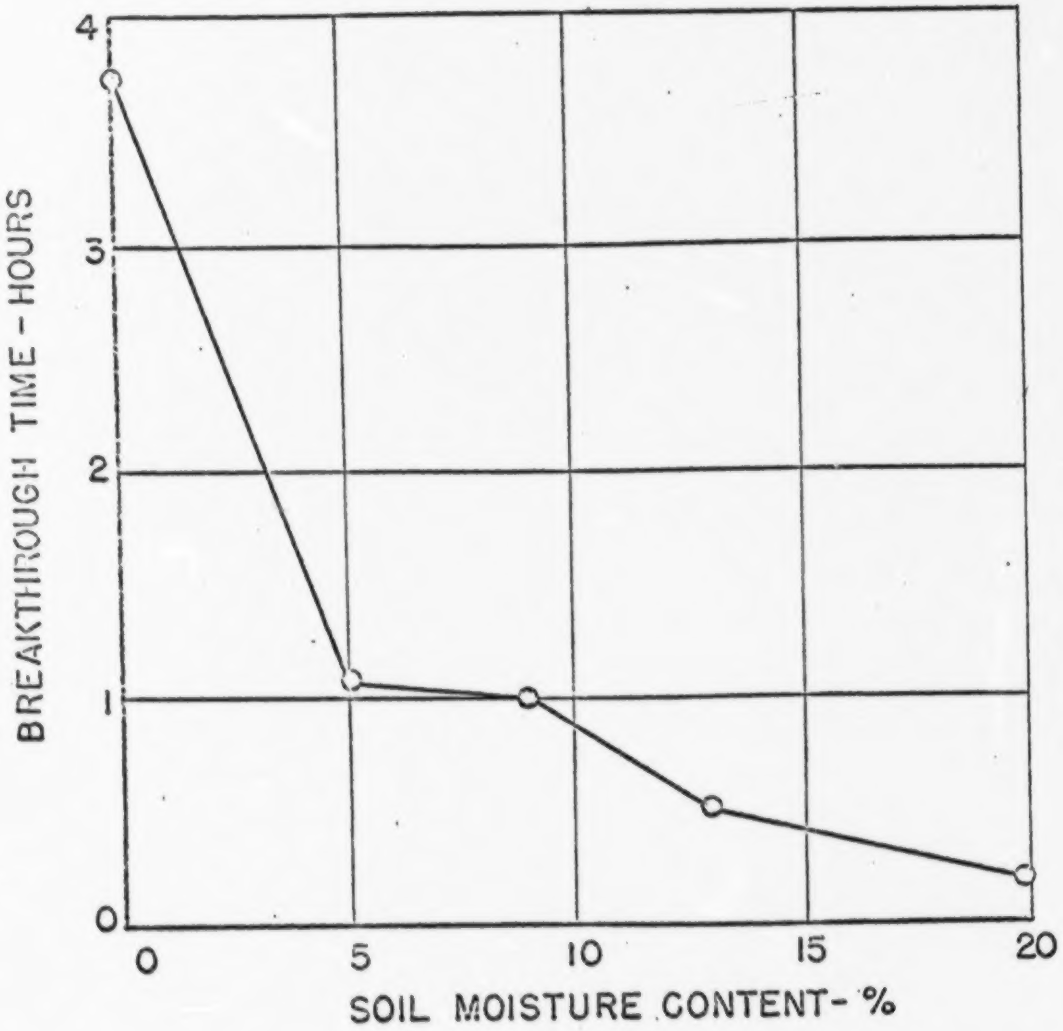
In the liquid-soil uptake studies, soil pH was varied by using three different pH buffering systems. The natural pH of the Lynden loam tested was 5.8. Uptake data was collected at pH values of 4.0, 5.8, and 8.0, Figure 2. This data shows that approximately equal removal occurs at pH 4.0 and 5.8, but also that much better removal occurs at pH 8.0. Either or both of two factors may have been responsible for this increase in sulfide removal ability at pH 8.0. (a) The predominant sulfide species present depends upon solution pH, as shown in Figure 22. At pH 5.8, aqueous hydrogen sulfide accounts for 90% of the total sulfur. Such changes in the predominant sulfur species present could be responsible for the variation in soil equilibrium removal capacity. (b) Changes in the ionization status of soil functional groups may also be responsible for the variation of removal capacity with pH. A change such as this in the ratio of attractive to repulsive forces could change the soil surface area through alteration of the physical structure of the soil.

Although the experimental evidence does not yield a definitive explanation for the better removal experienced in pH 8.0 liquid-soil systems, operation of a field scale installation using Lynden loam would be greatly enhanced at this pH. One method of operating at a pH different from the natural soil pH would be to buffer the soil at the desired pH. This would be extremely advantageous in small scale installations where infrequent maintenance is highly desirable. Another possibility would be intermittent



TOTAL FLOW - 3.91 ML./MIN./CM.^{2}
H_2S FLOW - 10 ML./MIN.
DETENTION TIME - 2.92 MIN.
TEMPERATURE - 25°C.
300 GRAMS OF DRY, STERILE,
P10 LYNDEN LOAM USED
IN EACH CASE

FIGURE 20 - EFFECT OF INFLUENT TEMPERATURE ON INITIAL BREAKTHROUGH TIME



TOTAL FLOW - 3.91 ML./MIN./CM.^{2}
H_2S FLOW - 10 ML./MIN.
DETENTION TIME - 2.92 MIN.
TEMPERATURE - 25°C.
300 GRAMS OF DRY, STERILE,
P10 LYNDEN LOAM USED
IN EACH CASE

FIGURE 21 - SOIL MOISTURE CONTENT INFLUENCE ON INITIAL H_2S BREAKTHROUGH TIME

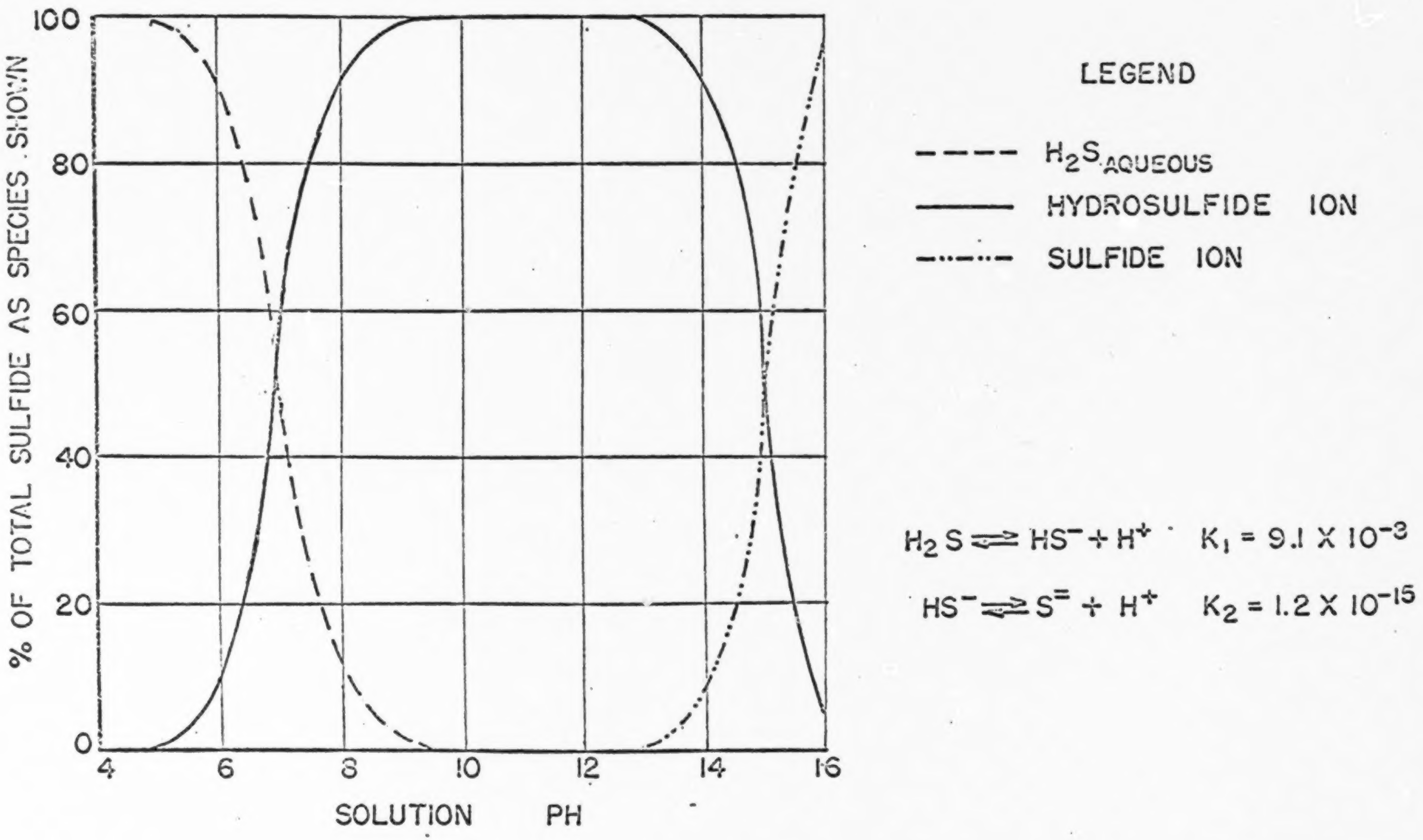


FIGURE 22 - CALCULATED CURVES OF SOLUTION PH INFLUENCE ON SULFIDE SPECIES PRESENT

spraying of a basic pH solution over the soil filter installation. This could possibly be practical for a large installation where a source of basic waste water is available, such as that resulting from the sodium hydroxide peeling of potatoes. The feasibility of this idea would have to be determined by further laboratory studies. An alternative possibility where a basic pH waste source is not available would be the use of alkaline soils. Although past research has shown that hydrogen sulfide removal by moist soil results in a decrease of soil pH, it is not possible at this time to determine the effectiveness of moist, alkaline soils for hydrogen sulfide removal.

Influence of Moisture Upon Dynamic Removal Situations

Because distinctly different mechanisms were found to be operative in moist and dry soils, the effect of moisture upon dynamic removal situations was studied. As shown in Figure 21, decreasing soil service times resulted from increasing soil moisture content. This decrease in breakthrough time may be attributed to any or a combination of several interdependent factors. (a) The ultimate capacity of a moist soil is less than that of a dry soil. (b) The rate of the removal mechanism in a moist soil is less than the removal rate in a dry soil. (c) Blockage of some of the soil interstices may have resulted from water addition. Regardless of the exact reason, it should be quite obvious that wherever possible, soil filters designed to remove hydrogen sulfide should be kept as dry as possible at all times.

Since dry soil evidenced better dynamic removal than moist soil it was felt unnecessary to further investigate the removal ability of moist soils. Therefore, all further dynamic studies utilized air dry soil. It should be noted that water vapor was a by-product of the removal reaction, although air passing through the soil removed this water, leaving the soil dry at all times.

Soil Rejuvenation in Dry Dynamic Removal Situations

All dynamic removal studies to this point were concerned solely with the time required for initial breakthrough of hydrogen sulfide, because this is the point normally necessitating filter replacement or rejuvenation. Therefore, the revivification capacity of the soil and conditions essential for revivification were the next aspects to be taken under consideration.

In Figure 17, the influence of the carrier gas upon removal is portrayed. This figure was obtained by maintaining a constant hydrogen sulfide flow, while the total flow through the column varied. As shown, use of an air carrier produced much longer soil service times than did a nitrogen carrier, other conditions remaining equal. To determine whether use of the nitrogen carrier made the removal mechanism completely inoperative, calculations were made to determine the initial breakthrough time assuming no interaction between the hydrogen sulfide and the soil, Appendix C. Table IX compares these calculated breakthrough times with those observed using nitrogen and air carriers, Figure 17.

TABLE IX: BREAKTHROUGH TIMES, OBSERVED AND CALCULATED, FOR A 10% H_2S CONCENTRATION

Total - $ml/min/cm^2$	Breakthrough Time - Hours		
	Calculated assuming no interaction with the soil	Nitrogen	Air
0.98	0.195	0.44	1.30
1.95	0.097	0.32	2.95
2.93	0.065	0.27	3.50
3.90	0.049	0.24	3.66
4.88	0.039	0.21	2.90
5.86	0.032	0.18	1.66

It is evident from this table that using a nitrogen carrier did not completely inhibit the removal of hydrogen sulfide, but the table also illustrates that using an air carrier gave much larger breakthrough times than did the nitrogen carrier. For example, at a total flow rate of 3.90-$ml/min/cm^2$ the breakthrough time using a nitrogen carrier was nearly five times longer than the calculated time assuming no interaction with the soil, but the breakthrough time using an air carrier was over fifteen times longer than when using the nitrogen carrier. Therefore, that use of a nitrogen carrier does not completely inhibit the total removal mechanism should be evident, but it should also be recognized that the presence of air definitely enhances the removal capacity of the soil.

The data presented in Table IX indicates that two operative removal mechanisms comprise the total removal system. The difference between the breakthrough times calculated assuming no interaction of hydrogen sulfide with the soil and the breakthrough times observed using a nitrogen carrier illustrate the effect produced by the first portion of the removal reaction. This first portion of the total reaction will be referred to as the "sulfidation" reaction, a term frequently used to describe the conversion of iron oxide to iron sulfide during the removal of sulfur compounds for natural gas.

The term sulfidation is only used at this time to refer to the first portion of the removal mechanism and is not meant to imply that iron oxides in the soil are the agents responsible for hydrogen sulfide removal. This initial reaction is followed by a rejuvenation reaction, which may be considered as an oxidation. This oxidation is responsible for the larger breakthrough times observed using an air rather than a nitrogen carrier. In summary, use of a nitrogen carrier allows only the sulfidation reaction to proceed, while use of an air carrier allows both the sulfidation and oxidation reactions to occur concurrently, resulting in more efficient soil utilization.

In the previously discussed testing, it was not known whether the rates of sulfidation and oxidation were equal to each other. To obtain this information, a 10% hydrogen sulfide mixture with an air carrier was passed through a column of dry soil until breakthrough, followed by removal of the soil from the column and exposure to room temperature air overnight. The following morning, the soil was repacked in the column and run again until breakthrough. The process continued until the breakthrough time experienced was 15 minutes. As shown in Figure 19, the breakthrough time of 15 minutes occurred after four rejuvenations of the soil. This behavior indicates that the rate of sulfidation is more rapid than the oxidation reaction at an H_2S concentration of 10%.

Removal of Sulfide from Liquid-Soil Systems

In the removal of sulfide from liquid-soil systems, it was necessary to determine initially the extent of removal which could be attributed to ion exchange. To investigate this possibility, chloride ions were exchanged for the exchangeable anions by shaking Lynden loam overnight in a 10% NaCl solution. The following morning, the liquid was decanted and the soil then washed three times with distilled water to remove any "free" ions. This washed soil was mixed with sodium sulfide and de-oxygenated pH 5.8 buffer, and then allowed to reach equilibrium with respect to sulfide removal. At this equilibrium point, no chloride ions were present in the liquid. Because no chloride ions were released during the sulfide removal, it is evident that the contribution of ion exchange in liquid-soil uptake is negligible.

It was also felt desirable to determine whether removal in liquid-soil systems could be the result of leaching of cations from the soil, followed by reaction of these leached cations with sulfide to form a precipitate. To ascertain this, a sample of Lynden loam was shaken overnight with pH 5.8 buffer. The next morning, the buffer and soil were separated, followed by one washing of the soil with distilled water. Uptake of sulfide at pH 5.8 was conducted on the washed soil and also on a liquid mixture consisting of the originally decanted buffer and the one distilled water washing. Results showed that this pre-treated soil removed exactly the same amount of sulfide as did a soil receiving no pre-treatment, but the system containing the decanted buffer and the distilled water washing removed no sulfide. Therefore, it is evident that removal of sulfide in liquid-soil systems occurs as the result of interaction with the soil, rather than reaction with leached cations.

When the results of the liquid-soil uptake data were plotted according to the Langmuir and Freundlich isotherm models, Figures 8 and 9, linear relationships were in evidence. Confirmation of these models reinforces the hypothesis that removal occurs at the soil surface, although not necessarily proving the hypothesis. It should be noted that no oxygen was present in the system during these uptake experiments, and therefore no rejuvenation of the soil by oxygen occurred.

Early experimentation with the addition of EDTA to a liquid-soil system indicated that removal of sulfide by wet soil could be completely inhibited by EDTA addition. This indicated the possible existence of a correlation between the maximum uptake capacity of EDTA by soil and the relative sulfide removal capacity. As shown in Table V, the soils tested are listed in order of their decreasing ability to remove sulfide at pH 5.8. The relative order of removal ability holds through the range of sulfide concentrations studied, Figures 4 and 7. The table illustrates the absence of any relationship between maximum EDTA uptake capacity or EDTA uptake per square meter of surface and the sulfide removal ability. The most probable explanation for this behavior may be attributed to the ability of EDTA to chelate, to some extent, all cations. In other words, EDTA chelates both cations associated with sulfide removal and those having no effect upon sulfide removal, therefore EDTA uptake results are not correlatable with sulfide removal. (Ringbom, 1963)

The linear relationships obtained in plotting the Freundlich and Langmuir isotherm models, Figures 8 and 9, further the hypothesis that removal of sulfide in liquid-soil systems occurs at the soil surface. Therefore, it was felt that a relationship might exist between soil surface area and the ability of the soil to remove sulfide from solution. But as shown in Table VII, no such relationship exists. For example, the clay studied had a relatively large surface area, 32 square meters per gram, but removed less sulfide than any of the other soils tested. Table VII also shows the elemental composition of the soils studied. Correlations were attempted for each soil between the relative ability to remove sulfide from solution and the following: Individual elements in the soil, groups of elements such as the heavy metals, alkali metals, and the alkali earth metals, and soil volatile matter. No correlations were found between these factors and the relative sulfide removal ability.

The scope of this research was intentionally restricted to several easily measured parameters in the endeavor to establish a simple correlation factor between the sulfide removal capacity of wet soils. The three factors which were considered are (a) soil surface area, (b) maximum EDTA uptake capacity, and (c) total soil composition. As previous discussions have shown, none of these factors correlated with removal ability, but isotherm evidence suggests that the removal mechanism is a surface phenomena. If such a removal mechanism does exist, a factor which must be considered in addition to surface area is the surface chemical composition. Due to the nonhomogeniety of most soil structures, the surface chemical composition could not be expected to agree with the bulk chemical composition. Unfortunately, measurements of soil surface composition involve highly sophisticated instruments and techniques, placing their utilization outside the simple guidelines considered in this research for soil comparisons.

Because elemental analysis gave no indication of which elements were most desirable at the surface for sulfide removal, twelve cation saturated soils were prepared as previously described. Each of these twelve soils had the exchangeable cations replaced by a known, but in each case different cation. It was felt that the relative removal ability exhibited by these twelve prepared soils could suggest the cations most and least desirable at the soil surface. As Figures 5 and 6 show, the relative removal ability of these twelve soils with respect to the replacing cation was Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}, Al^{+3}, Co^{+2}, Mg^{+2}, Mn^{+2}, Ca^{+}, Na^{+}, K^{+} and Ba^{+2}. It should be mentioned that only the most oxidized form of each element was used in these saturation studies. From the standpoint of overall improvement in soil removal capacity Cu^{+2}, Fe^{+3}, Zn^{+2} and Ni^{+2} appear to be those cations most desirable at the soil surface. Unfortunately, analysis of the total soil chemical composition yields no indication of the percentage of these elements available at the soil surface.

In summary, the easily measured parameters which were initially selected to relate the sulfide removal capability of wet soils produced no meaningful results. But, uptake tests using soils with known cations replacing the exchangeable cations at the soil surface indicate that Cu^{+2}, Fe^{+3}, Zn^{+2} and Ni^{+2} are the elements most desirable at the soil surface. At the current time, it is felt that the easiest available method to determine the sulfide removal ability of wet soils is to run a batch uptake test similar to that described within this research.

Hydrogen Sulfide Removal in Static Gas-Soil Systems

Static gas-soil testing used either of four gases in combination with hydrogen sulfide. These gases were air, oxygen, carbon dioxide, and nitrogen. As portrayed in Figure 12, use of air or oxygen produced identical hydrogen sulfide removals, while tests using nitrogen or carbon dioxide gave removal identical to each other, but substantially lower removal than oxygen or air. This behavior points out the importance of oxygen, or the oxygen component of air, in rejuvenation of the soil. In fact, the difference between the amount of removal with oxygen present and without oxygen present indicates the extent of rejuvenation at the temperature and concentration under study. For example, Figure 12 shows that P200 Lynden loam at 20°C and an equilibrium hydrogen sulfide concentration of 4500 ppm was rejuvenated approximately two and one-half times.

Any relationship between hydrogen sulfide capacity and the maximum EDTA removal capacity, measured in a liquid-soil system would appear to be invalid due to the rejuvenation ability of the soil, when in contact with oxygen. In other words, although one EDTA molecule may be capable of chelating only one removal "site", this same "site" could take up any number of hydrogen sulfide molecules, depending upon factors to be considered later. In addition, EDTA chelates many different cations, some most likely not even responsible for hydrogen sulfide removal. As seen in Table VI, no relationship exists between the capacity of a soil to remove EDTA from solution and to remove hydrogen sulfide from air. (Ringbom, 1963)

Table VIII shows the soils studied, listed in order of their decreasing ability to remove hydrogen sulfide, and the elemental composition of these soils. No relationship exists between the ability of these soils to remove hydrogen sulfide and any element, group of similar elements, or the soil volatile matter content. However, a relationship does appear between the hydrogen sulfide removal ability and the multiple of soil surface area per gram and the weight percentage of iron in the soil. Comparing this relationship with the hydrogen sulfide equilibrium uptake capacity at 5550 ppm, shown in Table VIII, indicates that the relationship is far from quantitative. In other words, the ratio of

$$\frac{\text{\% iron x surface area / gram of soil}}{\text{ML of } H_2S \text{ removed / gram of soil}}$$

is not quantitative, as shown in Table VIII. For example, at an equilibrium concentration of 5550 ppm, P200 clay gave a ratio of 2.08 while P200 Lynden loam gave a ratio of 12.9, in spite of the clay's ability to remove more hydrogen sulfide than Lynden loam. Lack of such a quantitative relationship lends doubt to both the validity and practicality of comparing soils in this manner. Another factor which casts doubt upon this relationship is the requirement that the soil elemental composition remain homogenous throughout the soil structure. This is highly doubtful in soils such as clay and humus, which are negatively charged and surrounded by a layer of charge neutralizing cations.

As previously noted, the Freundlich isotherm model normally best describes multilayer adsorption, whereas the Langmuir model was derived assuming monolayer adsorption upon a surface of identical removal sites. In the uptake of hydrogen sulfide by chemisorption, with rejuvenation of the removal "sites" by oxidation, removal could be pictured as similar to multilayer adsorption, even though the soil surface is not covered. As seen in Figure 12, plotting the observed results according to the Freundlich model yields a linear relationship over the range of concentrations studied. Conversely, the Langmuir model, Figure 13, does not yield a linear relationship for the same data. This behavior appears to indicate that a possible multilayer buildup of sulfur atoms is deposited adjacent to the removal site.

As previously explained when discussing liquid-soil removal, it was felt that running a series of tests using different soils, each having all exchangeable cations replaced by a known cation, would demonstrate which cations were responsible for hydrogen sulfide removal. As Figures 14 and 15 show, the cations listed in order of their decreasing effectiveness were Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}, Al^{+3}, K^{+}, Ca^{+2}, Na^{+}, Mg^{+2}, Ba^{+2}, Mn^{+2} and Co^{+2}. Valences shown are the valence of the cation originally used when replacing the exchangeable cations. The latter six of these either only slightly improved the soil's capacity for hydrogen sulfide, or even slightly decreased it, in relation to the "washed" control.

On the basis of the results observed, the ability of the soil to be rejuvenated is readily observable. It also appears evident that oxygen is the gaseous agent responsible for this rejuvenation. Therefore, a mechanism as shown below appears to be responsible for the sulfidation phase of the removal mechanism

$$MO_x + XH_2S \longrightarrow MS_x + XH_2O$$

where M is the cation responsible for the existence of the removal "site". Once this reaction has proceeded, the presence of oxygen in the gas phase oxidizes this sulfided "site". This oxidation reaction may be visualized as

$$2MS_x + XO_2 \longrightarrow 2MO_x + \text{SULFUR}$$

At this point, the "site" has been rejuvenated one time and is available for further sulfidation. Such sulfidation and oxidation reactions proceed continually at each "site" contacted by hydrogen sulfide and oxygen, the overall reaction rate depending upon hydrogen sulfide concentration, reaction zone temperature, and soil moisture; while the total capacity depends upon the soil's capacity to accept the deposited sulfur. Rather than being simply a chemisorption reaction, a more appropriate definition would be contact or surface catalysis, consisting of a sulfidation and oxidation reaction.

A sulfur mass balance was conducted for a soil column containing 300 grams of dry soil operated under the following conditions: inflow temperature - 25°C, H_2S concentration - 10%, total flow rate - 100 ml/min, and an air carrier. Breakthrough time for this column was 3.66 hours, calculations showed that by the time breakthrough occurred 3.06 grams of H_2S had entered, or 0.0102 grams of sulfur per gram of soil. An extraction of sulfur from a uniform mixture of soil gave 0.0100 grams of sulfur per gram of soil. A test was conducted for sulfate ion in this same soil, but none was present. This sulfur mass balance closes within 2.0% between calculated figures and the observed data.

The Suggested Method of Design Optimization

The information gathered in the dynamic uptake phase of this research was intentionally limited in the range of concentrations and soil depths studied. This limitation was necessary, since the purpose of the research was the establishment of a method of design optimization and a study of revivification ability, rather than a solution to the design for a particular situation. Therefore, it is not suggested that the results obtained in this limited study should be used directly for application to a field scale installation. Rather, it is suggested that a bench scale study utilizing the actual, or a synthesized air stream to be purified be used for a similar method of data collection and presentation in order to follow the recommended procedure for design optimization.

To operate soil filters removing H_2S from air streams in the most economical fashion, a method of design optimization must be developed to utilize the removal capacity of a soil in the most efficient manner. As Figure 19 illustrates, soil possesses a revivification ability, although breakthrough times are successively shorter as the number of rejuvenations increases. This shortening of breakthrough time indicates the existence of a maximum soil removal capacity. The most efficient mode of operation would therefore be directed toward achieving a minimum "down time" for soil rejuvenation. To achieve this minimum "down time," the total flow rate per square foot of surface which yields the maximum removal of H_2S prior to breakthrough should be selected. Operation in this manner will allow optimum time utilization of all facilities involved in the operation, such as land, labor, soil holding chambers, pumps, and electrical power.

Before presenting the method of design optimization, a brief discussion of the relevant factors in dynamic removal systems and their inter-relationships will be discussed. Five principal factors influence dynamic removal: (a) detention time, (b) reaction temperature, (c) quantity of hydrogen sulfide entering, (d) initial hydrogen sulfide concentration, and (e) total flow rate per square foot of soil surface. The first three of these will be discussed in the following paragraphs in terms of the latter two and other pertinent factors.

(a) Detention time - Detention time within a soil filter must be sufficiently long to permit all of the hydrogen sulfide to contact a removal site, and also long enough to prevent channeling through the soil. Detention time per unit depth is a function of the total flow rate per square foot of surface and the soil voids ratio.

(b) Reaction temperature - Significance of the reaction temperature is readily portrayed by Figure 20. Although the reaction with dry soil is exothermic (see temperature data in Appendix J) the reaction rate increases with increasing temperature, therefore enhancing the removal efficiency of the soil prior to breakthrough. The reaction temperature is dependent upon the ambient temperature, the total flow rate per square foot, and the amount of hydrogen sulfide entering per unit time.

(c) Quantity of H_2S Entering per Unit Time - At any concentration, the reaction temperature increases as the amount of hydrogen sulfide entering increases, as shown by the temperature data in Appendix j. The quantity of hydrogen sulfide entering is a function of H_2S influent concentration and the total flow rate per square foot of soil surface.

The first step in the design process involves obtaining from bench scale studies a curve of breakthrough time versus the total flow rate per square foot of surface for the gas stream to be purified. It is recommended that the depth of soil utilized in this bench scale testing be the maximum possible available for the full scale installation. This allows for a maximum amount of upward travel of the removal zone prior to breakthrough.

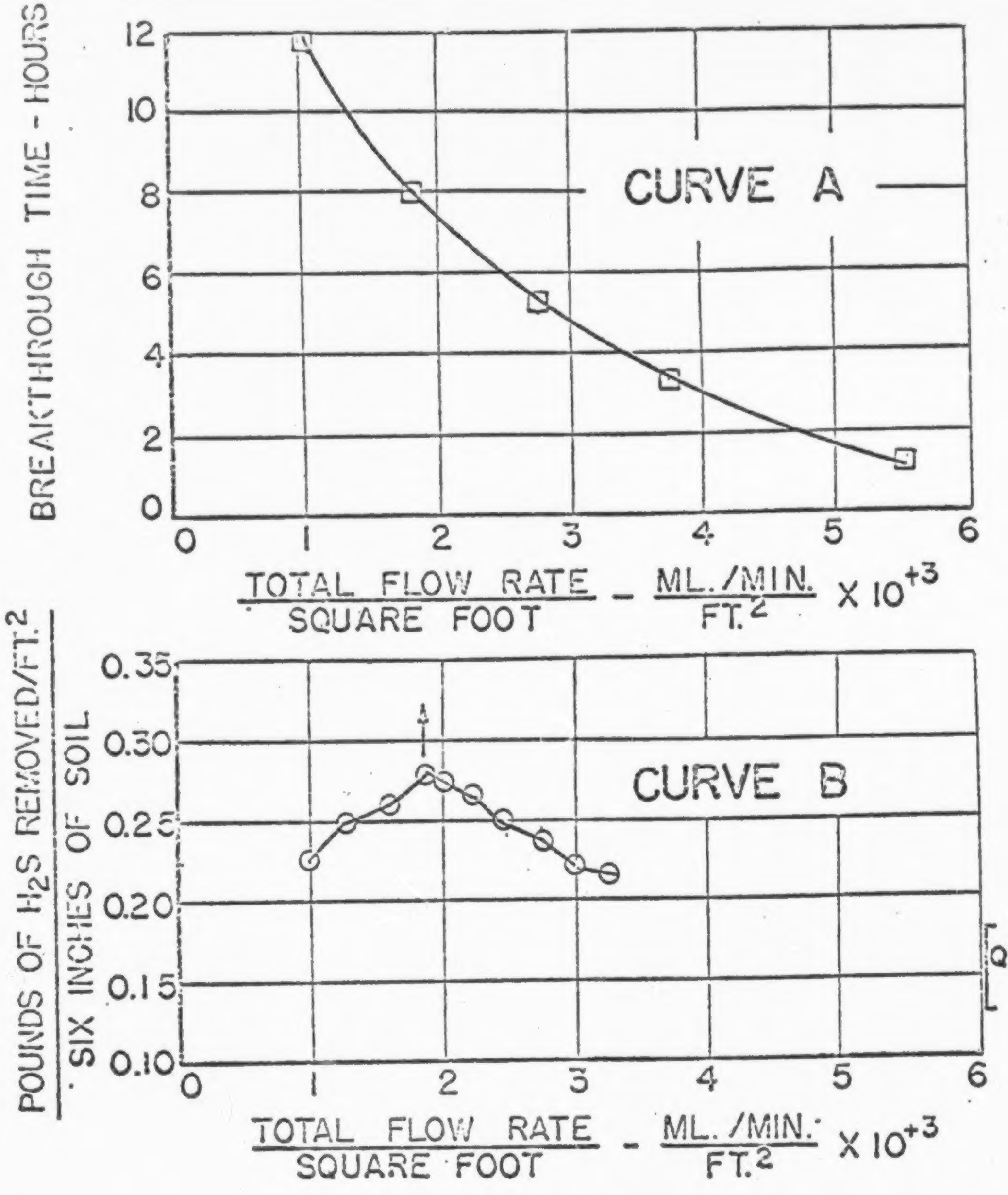
The upper curve (Curve A) of Figure 23 illustrates such a plot of breakthrough time versus total flow rate per square foot of soil surface, obtained from data presented in Figure 16 for a six inch soil depth. Using information from Curve A, a plot (Curve B) of weight of hydrogen sulfide removed per six inch soil depth versus total flow rate per square foot should be plotted directly below. For an example of this calculation, consider the flow of 1750 ml/min/ft^2 which yielded a breakthrough time of 8.4 hours.

Therefore:

$$\frac{\text{lb. } H_2S \text{ removed/ft}^2}{\text{6 inches of soil}} = (1750 \text{ ml/min/ft}^2)(0.1 \frac{\text{ml } H_2S}{\text{ml total}})(60 \text{ min/hr})(8.4 \text{ hr})$$

$$(0.307 \times 10^{-5} \frac{\text{lb. } H_2S}{\text{ml } H_2S})$$

$$\frac{\text{lb. } H_2S \text{ removed/ft}^2}{\text{6 inches of soil}} = 0.279 \text{ lb.}$$



CONDITIONS FOR CURVE A

TEMPERATURE - 25°C.
H_2S CONCENTRATION - 10%
300 GRAMS OF DRY, STERILE,
P 10 LYNDEN LOAM USED
IN EACH CASE

POINTS FOR CURVE B WERE OBTAINED USING THE EQUATION:

$$\frac{\text{POUNDS OF } H_2S \text{ REMOVED/FT.}^2}{\text{SIX INCHES OF SOIL}} =$$

$$\left[Q_{TOTAL}\right]\left[\frac{H_2S \text{ CONC.}}{100}\right]\left[60\,\frac{\text{MIN.}}{\text{HR.}}\right]\left[3.07 \times 10^{-6}\,\frac{\text{LB. } H_2S}{\text{ML. } H_2S}\right]\left[\text{BREAK. TIME}\right]$$

FIGURE 23 - METHOD OF DESIGN OPTIMIZATION

Using Curve B, the optimum total flow rate per square foot is conveniently chosen as the flow rate yielding the maximum pounds of hydrogen sulfide removed prior to breakthrough. Using this flow rate per square foot, the number of square feet of surface required at the depth tested can be calculated by dividing the total flow rate of the gas stream to be purified by the optimum flow rate per square foot chosen in the design study.

Mechanisms

On the basis of the data herein presented, it is possible to postulate mechanisms which describe the removal of S(II) species on soil in both wet and dry conditions.

Wet Soil Removal Mechanism

Removal of sulfide from solution by soil is an endothermic process. Ion exchange is not a factor in removal, moreover agreement of experimental data with the Freundlich and Langmuir isotherms suggest that adsorption is the responsible removal mechanism. Better removals were obtained at pH 8.0 than at pH 4.0 or 5.8, suggesting that hydrosulfide ion and not H_2S (aq) is the active species. Removal is enhanced by the presence of certain cationic species at the soil surface (Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}).

Dry Soil Removal Mechanism

Removal of high concentrations of hydrogen sulfide gas by dry soil is a two stage process which is best defined as surface catalysis. Initially hydrogen sulfide reacts with a removal site, according to

$$MO_x + XH_2S \longrightarrow MS_x + XH_2O$$

where MO_x is the cation oxide present at the removal site. In the presence of oxygen, the site is rejuvenated as shown

$$2MS_x + XH_2O \longrightarrow 2MO_x + \text{SULFUR}$$

It is believed that the limitation on the number of possible rejuvenations is due to steric hinderance caused by the deposition of sulfur at the removal site. The cations most desirable at the soil surface are Cu^{+2}, Fe^{+3}, Zn^{+2} and Ni^{+2}.

Dynamic Removal Optimization

Removal of high concentrations of hydrogen sulfide from moving air streams is performed much more efficiently by dry soil than wet soil. Interrelated parameters which influence the removal of hydrogen sulfide by dry sterile soil are detention time, reaction temperature, amount of hydrogen sulfide entering, concentration of hydrogen sulfide, and the total flow rate.

A method of design optimization is presented (Figure 23) which determines for a given concentration and influent gas temperature, the total flow rate at which the maximum removal of hydrogen sulfide per unit time results. It is felt that this design optimization method should be restricted to air streams containing only hydrogen sulfide, until further research delineates the removal mechanism for other odorous gases.

BIOLOGICAL ASPECTS OF SOIL FILTER ACTIVITY

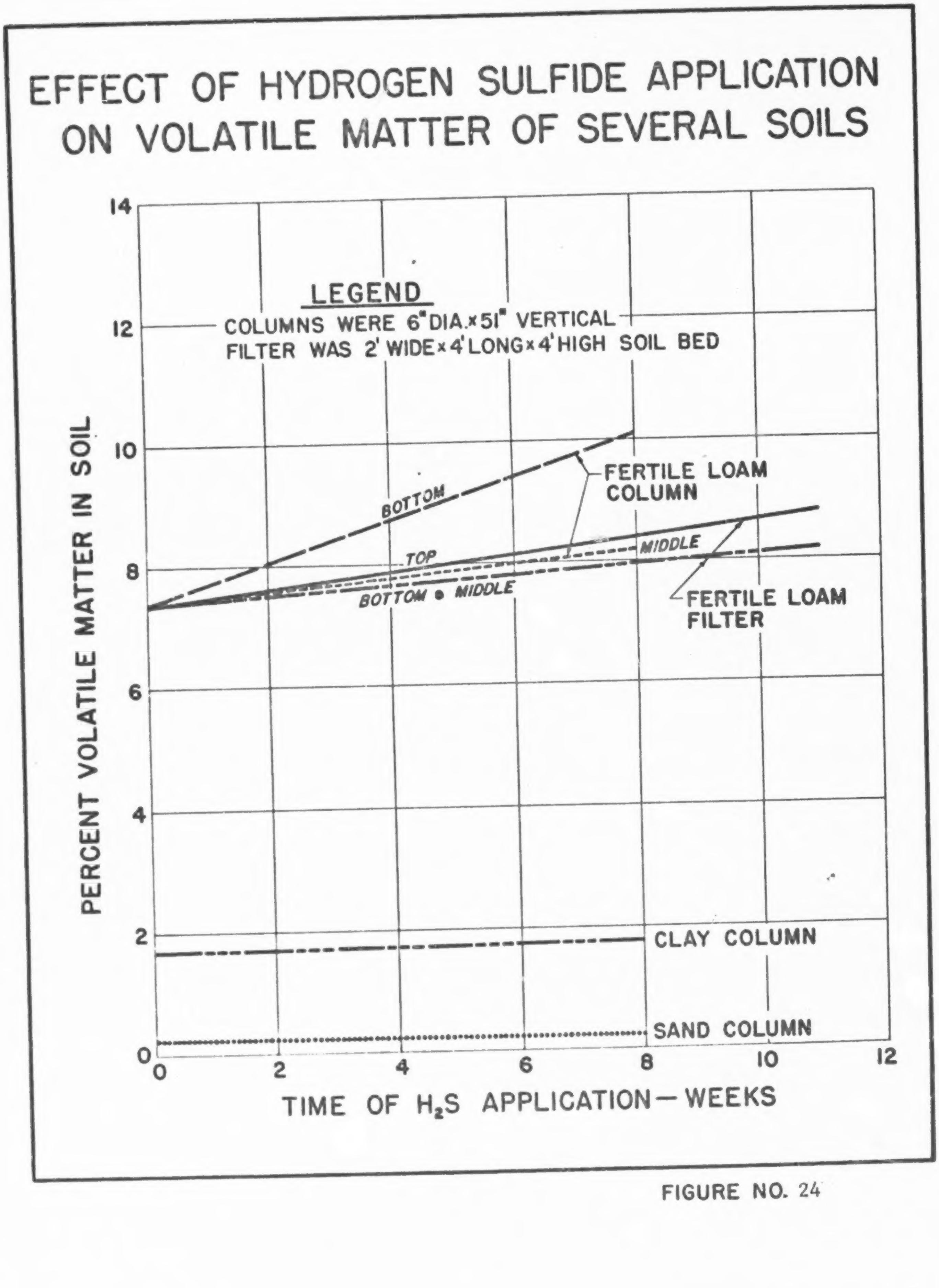
For relatively low concentrations, up to 100 mg/l, soil filter biological populations remain active in the presence of hydrogen sulfide gas transmitted in air streams through the filter. Studies on the gas stabilization abilities of biological populations proceeded under this project for several years. Investigations on the populations inhabiting the filters are reported in Appendix A. Engineering aspects of the filter are covered in this section.

Filter studies in the laboratory were conducted in soil containing chambers and in six inch diameter plexiglas columns. Teflon lined sealed plywood chambers were 2 feet wide by 4 feet long by 4 feet high. The test gas and air were added to the gravel underspace of these soil filters. The three inch gravel underlayer assisted in diffusion of the gas across the filter area. In the 6 inch diameter columns, three neoprene discs with 4 inch concentrically located openings were spaced up through the column to prevent sidewall channeling. Gas sampling ports were provided along the sides of the filters. Soil sampling was accomplished by removing soil from these 1 inch diameter ports. Hydrogen sulfide, methyl mercaptan and methane removal were tested in various soil types.

Test Results with Hydrogen Sulfide

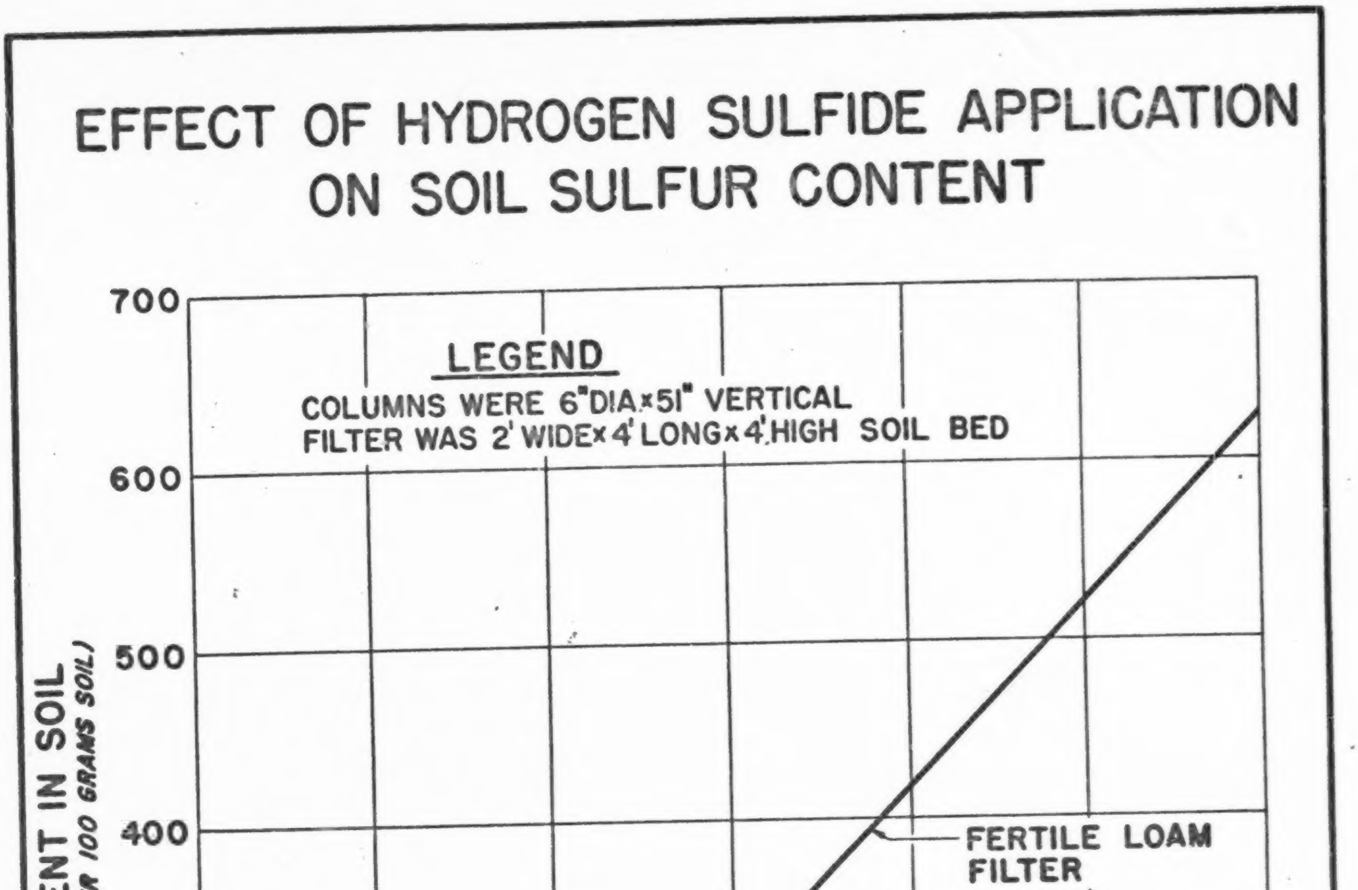
Several types of soil were used: fertile loam, both moist and completely dried, clay gravel soil and Ottawa sand. The loam was an enriched soil from the University of Washington greenhouse, the clay gravel soil was from the Seattle freeway site. Over a two month period of application of hydrogen sulfide, the liquid limit of the soils decreased. During this time the total volatile material increased significantly in the moist fertile loam while little or no increase occurred in the clay or sand columns, as shown in Figure 24. Coincidently with the volatile-matter increase the sulfur content in the loam rose markedly while in the sand column no increase in sulfur content occurred (Figure 25). Elution of the loam filter with water draining down through the soil indicated a sulfur removal of 1.2 mg S/wk in 10 l of elution water. However, the net gain of some 600 mg S/100 g of soil over a 3-month test period indicates that the loss of sulfur by elution is negligible. When the soil was removed from the filter box at the end of the of the test period, the lower soil regions, and especially the bottom inch, were considerably lighter in color than the remainder of the soil column. Deposits of a yellow-white material were discovered. This material was found to be an amorphous mixture of various precipitated minerals including sulfur.

In field tests of the Mercer Island pumping station, using soil filters for odor reduction, Mayo (1962) found a maximum back pressure of 1.25 in. (3.2 cm) of water for a soil column of 30 in (76 cm) and a gas flow of 1 cfm/sq ft (0.305 cu m/min/sq m). Table X present the effects of moisture and soil depth on back pressures at various flow rates and indicates a maximum back pressure of 2.4 in. (6.1 cm) of water for 32 in. (81 cm) of fertile loam under saturated conditions.



EFFECT OF HYDROGEN SULFIDE APPLICATION ON VOLATILE MATTER OF SEVERAL SOILS

FIGURE NO. 24



EFFECT OF HYDROGEN SULFIDE APPLICATION ON SOIL SULFUR CONTENT

FIGURE NO. 25

TABLE X.

Back Pressure Variation with Soil Depth and Moisture Content

Flowrate	Moisture	Soil Depth[2]			
		32"	21"	10"	0"
77 l/min or 0.34 cfm/ft^2	Dry	0.9"[3]	1.3"	1.0"	0.4"
	Moist	1.4"			
	Saturated	2.4"			
43 l/min or 0.19 cfm/ft^2	Moist	0.7"	0.6"	0.5"	0.1"
15 l/min or 0.07 cfm/ft^2	Moist	0.3"	0.2"	0.1"	0.1"

---

[1] Cross sectional area of filter is 8 ft^2.

[2] 5" of coarse gravel covers perforated discharge pipe. Soil depth refers to depth of soil above gravel.

[3] Pressure given in inches of water.

Figures 26, 27 and 28 reveal how hydrogen sulfide concentrations are reduced by contact with the soil. Figure 26 indicates that about 90 percent of the odor reduction occurs in the first 2 ft (0.6 m) of the soil column. The remaining few inches of soil are required to reduce the hydrogen sulfide to a concentration below the threshold odor limit in the air stream emanating from the surface of the soil filter.

Figure 27 indicates that for the moist organic soils there is no reduction in the odor-removing potential of the soil over the span of time the tests were run. However, the ability to remove hydrogen sulfide decreased with application time for the clay, sand, and oven-dried loam filters.

Figure 28 presents the results of a test of effectiveness of hydrogen sulfide removal with increasing input concentrations to the soil column. In general, as the input concentration of H_2S increased, the percent removal increased.

Tests were run on the elution water which was passed through the soil column. The elution rate was 10 l/wk. As shown in Figure 29, in all soil beds tested the pH dropped during the period of hydrogen sulfide application. In the loam soils the pH value reached a low of 2.5 by the end of the test period.

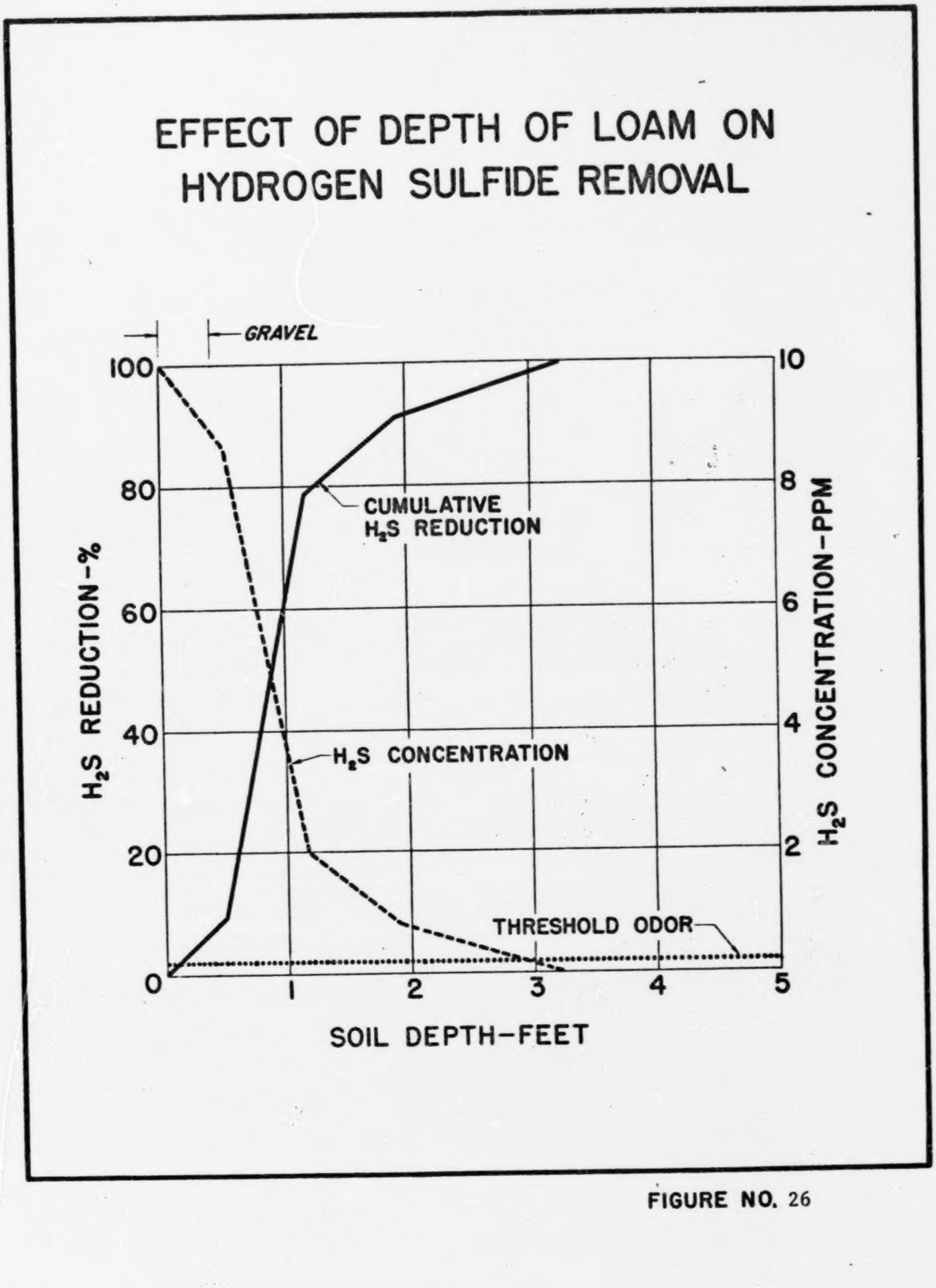
Without application of hydrogen sulfide, the elution water ion concentrations should drop gradually toward the ion concentrations in the water before application to the bed. However, the biological oxidation of sulfide to sulfate in the moist loam filters resulted in increases in sulfate concentrations in the elution water and a resultant increase in conductivity of the elution water. For example, in the loam filter box the increase in sulfates changed from 298 mg/l SO_4 at the beginning of the test period, to 2,120 mg/l SO_4 after 3 wk of H_2S application, and to 5,760 mg/l SO_4 after 11 wk. For the clay sand columns, the increases in SO_4 concentrations were about the same at the beginning and at the end of the 8-wk test period. For the clay columns, sulfate concentrations were 230 and 287 mg/l and for sand 148 and 158 mg/l at the beginning and end of the test periods.

The tests run on the sand and clay indicate that these materials are not satisfactory for use in soil filters. The filter material must act as a base for good biological growth and also must allow easy passage of moisture down through the soil and the passage of gases up the column.

With the addition of nutrients, materials such as vermiculite or synthetic products might serve well as filters by providing a loosely packed material which could facilitate gas and water flow.

Recycle Batch System for Evaluation of Microbial H_2S Removal

A closed system for recycling gases through a soil sample was designed as shown in the flow diagram below. The whole system acts as a closed unit with an initial slug of hydrogen sulfide added to the system and then recycled through the soil sample. The tests were run with moist 10 gram aliquots of soil taken from the enriched sandy loam at the University of Washington greenhouse. The soil was placed in the cylindrical soil filter chamber at the



EFFECT OF DEPTH OF LOAM ON HYDROGEN SULFIDE REMOVAL

FIGURE NO. 26

EFFECT OF APPLICATION PERIOD ON HYDROGEN SULFIDE REDUCTION BY VARIOUS SOILS

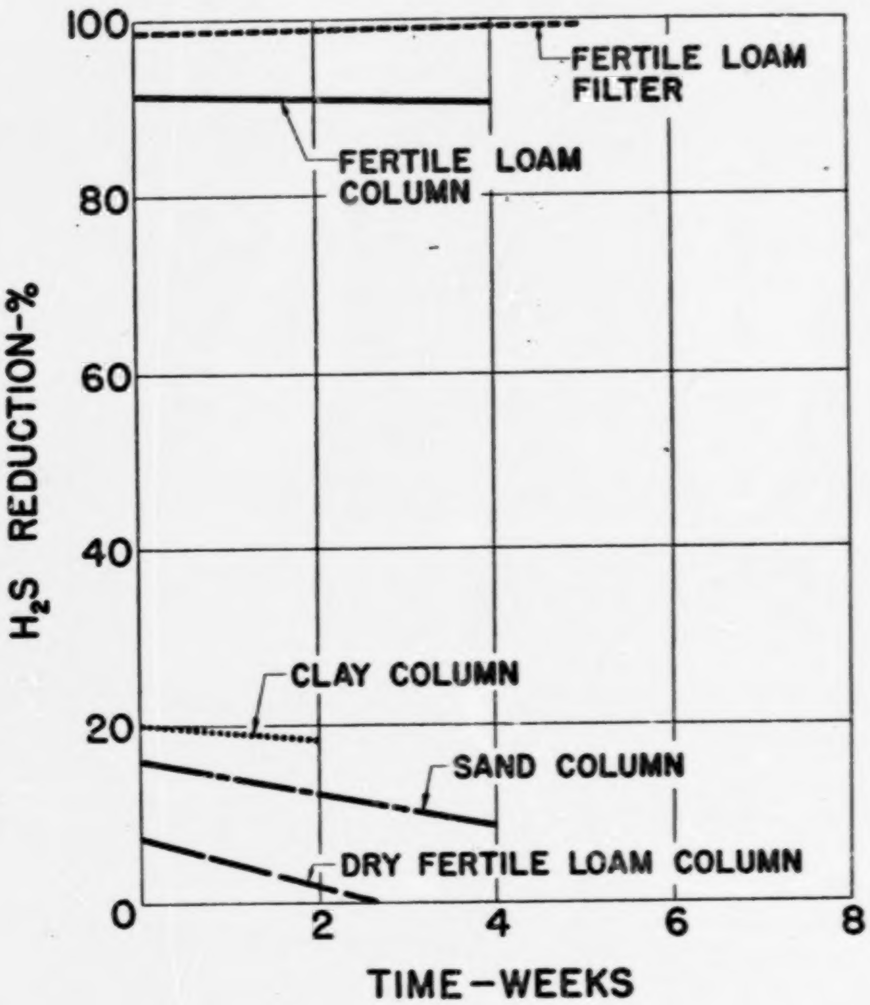
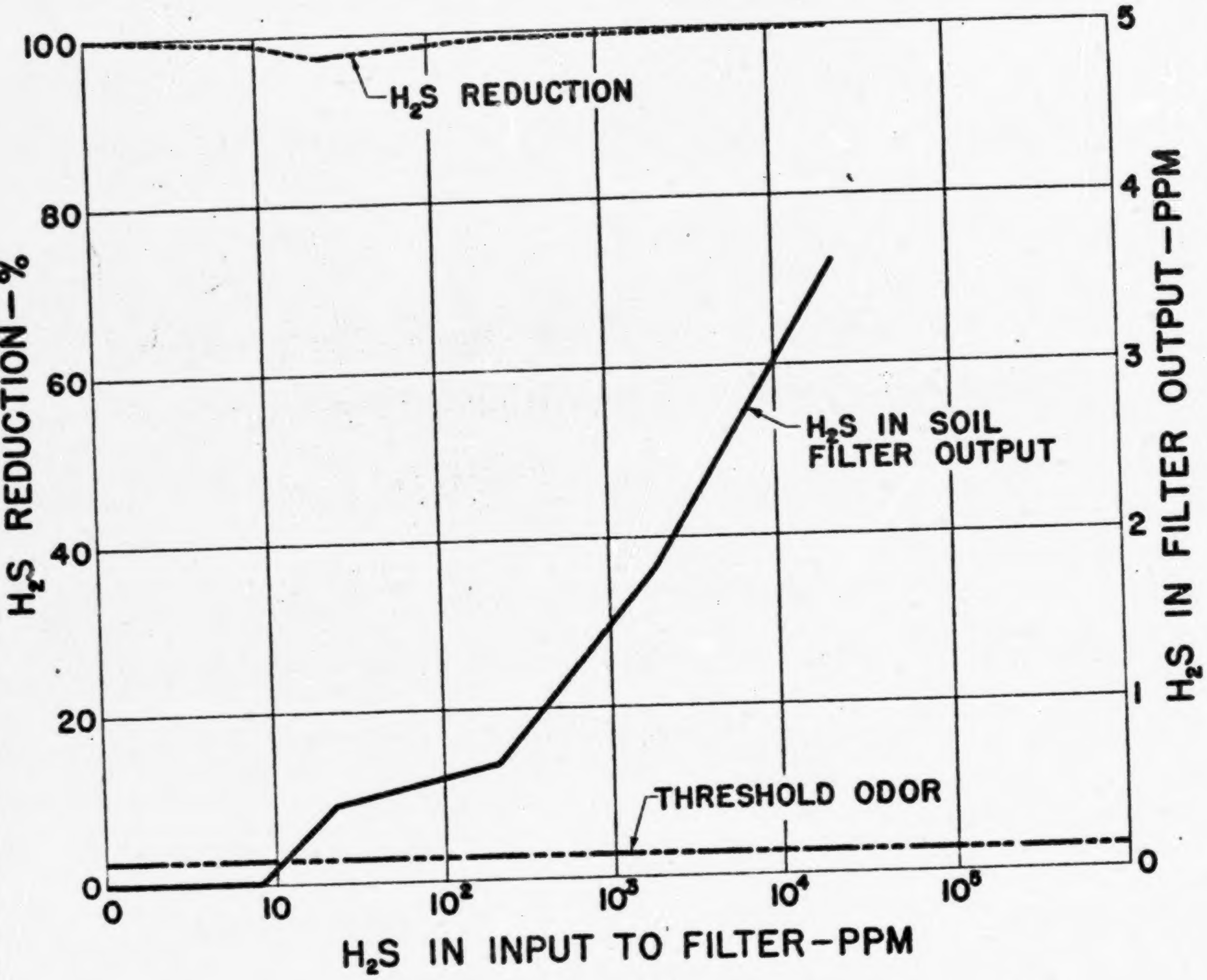


FIGURE NO. 27



EFFECT OF INPUT CONCENTRATION ON HYDROGEN SULFIDE REMOVAL EFFICIENCY BY SOIL FILTERS

FIGURE NO. 28

EFFECT OF APPLICATION TIME ON FILTER BED $_{p}H$

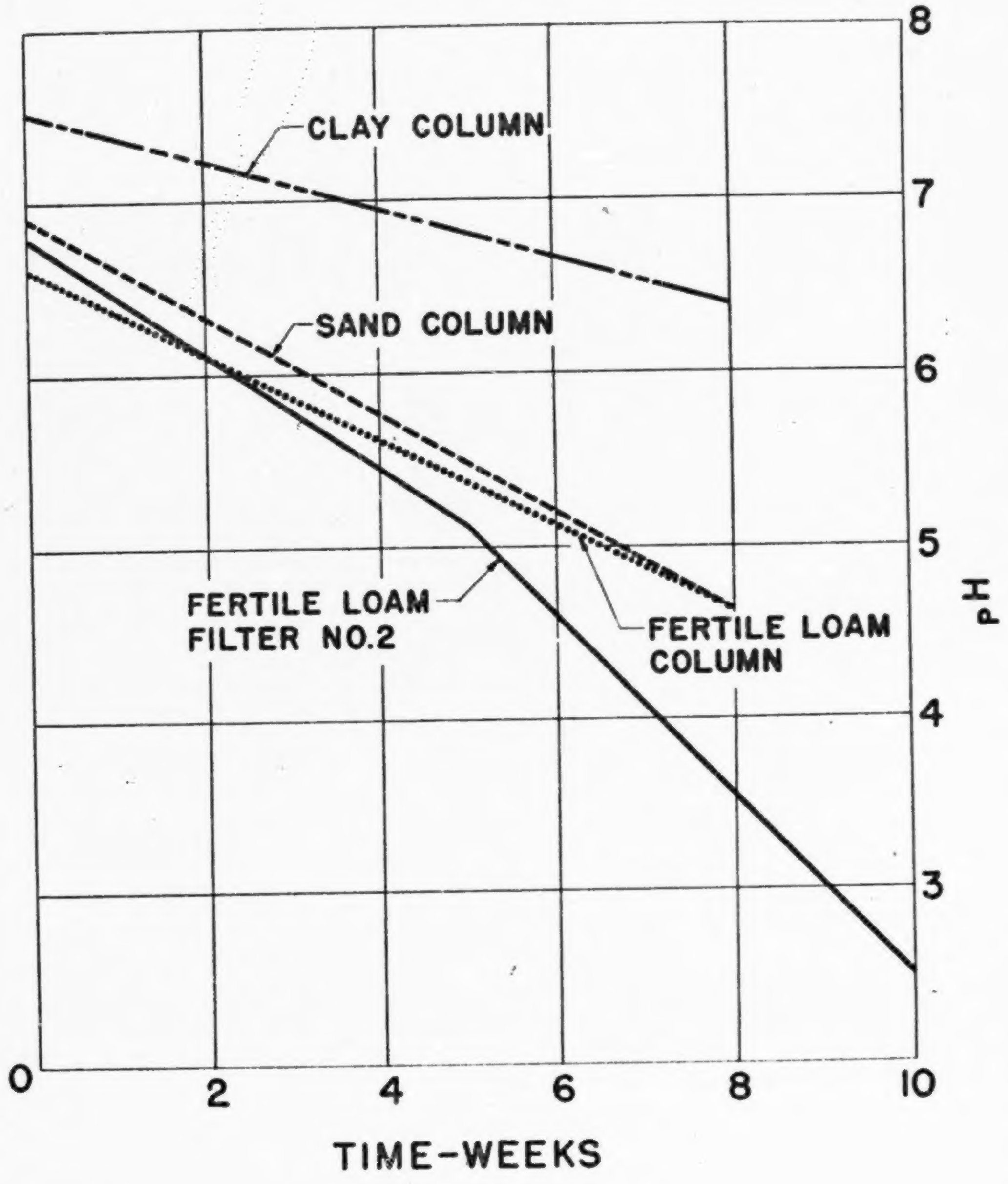


FIGURE NO. 29

left in Figure 30. The soil filter chamber is 2.5 cm in diameter and 5 cm deep. The experiments were performed at room temperature with moist soil particles passing a U.S. Standard No. 12 sieve. Soil water content was 20%.

At a flow rate of 40 cm^3/hour/cm^3 cross sectional area of the soil filter column (about one cycle per hour) and with an initial hydrogen sulfide concentration of 720 mg/l, a unit with microorganisms acclimated by previous exposure to hydrogen sulfide had an initial removal of hydrogen sulfide of 80% in the first cycle through the soil filter while a corresponding unit with sterilized soil had a 35% removal. At the end of 9 hours of recycling the residual H_2S concentrations were 2.5% for the soil containing microorganisms and 16.5% for the sterile unit. At 15 hours 15% of the H_2S remained in the sterile unit while in the other unit all the H_2S had been removed.

At the high dosage used in this experiment many of the less tolerant microorganisms were no longer viable on agar media. Only two bacterial colonies appeared on the plates.

The ability of microorganisms to enhance hydrogen sulfide removal is evidenced also in Figure 31 which shows significantly better removal with microorganisms present and shows somewhat better removal with organisms previously exposed to hydrogen sulfide.

Figure 32 shows the improvement in removal when soil moisture is present. Note the deleterious effect of drying on the removal rate. Note also that even at 10.5% moisture removal rates are increased in the presence of microorganisms.

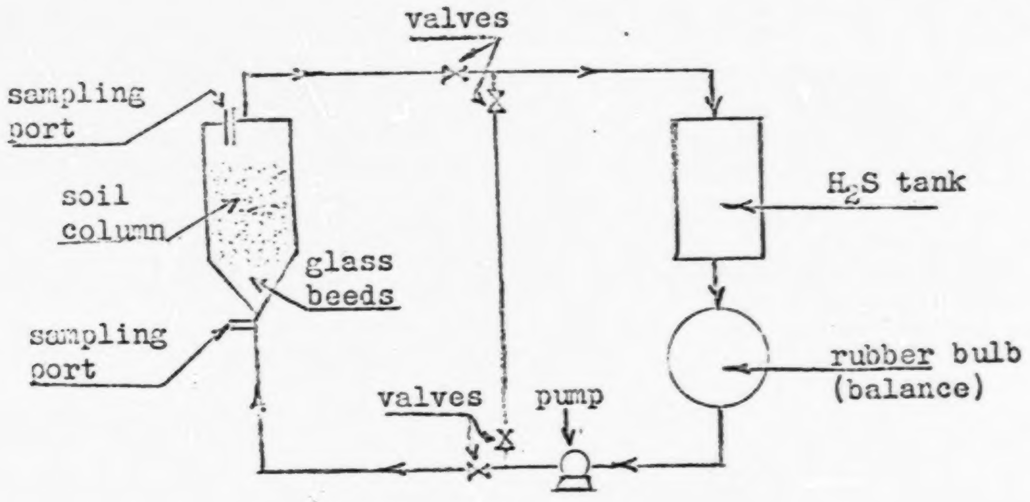


Figure 30 - Flow Diagram for Batch Recycle System for Soil Filter Removal of Hydrogen Sulfide

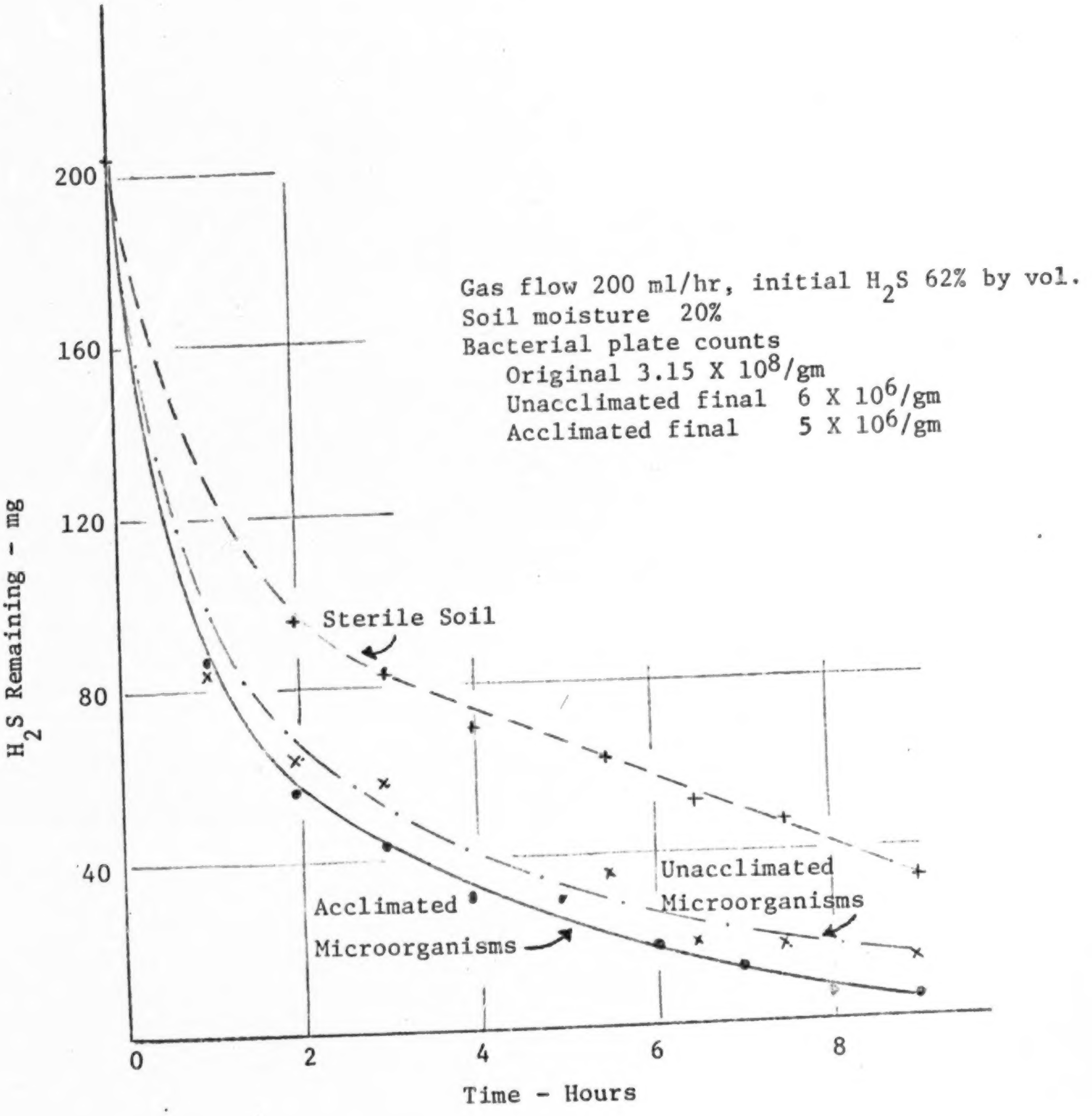


FIGURE 31 - EFFECT OF MICROORGANISMS ON REMOVAL OF HYDROGEN SULFIDE IN SOIL FILTERS

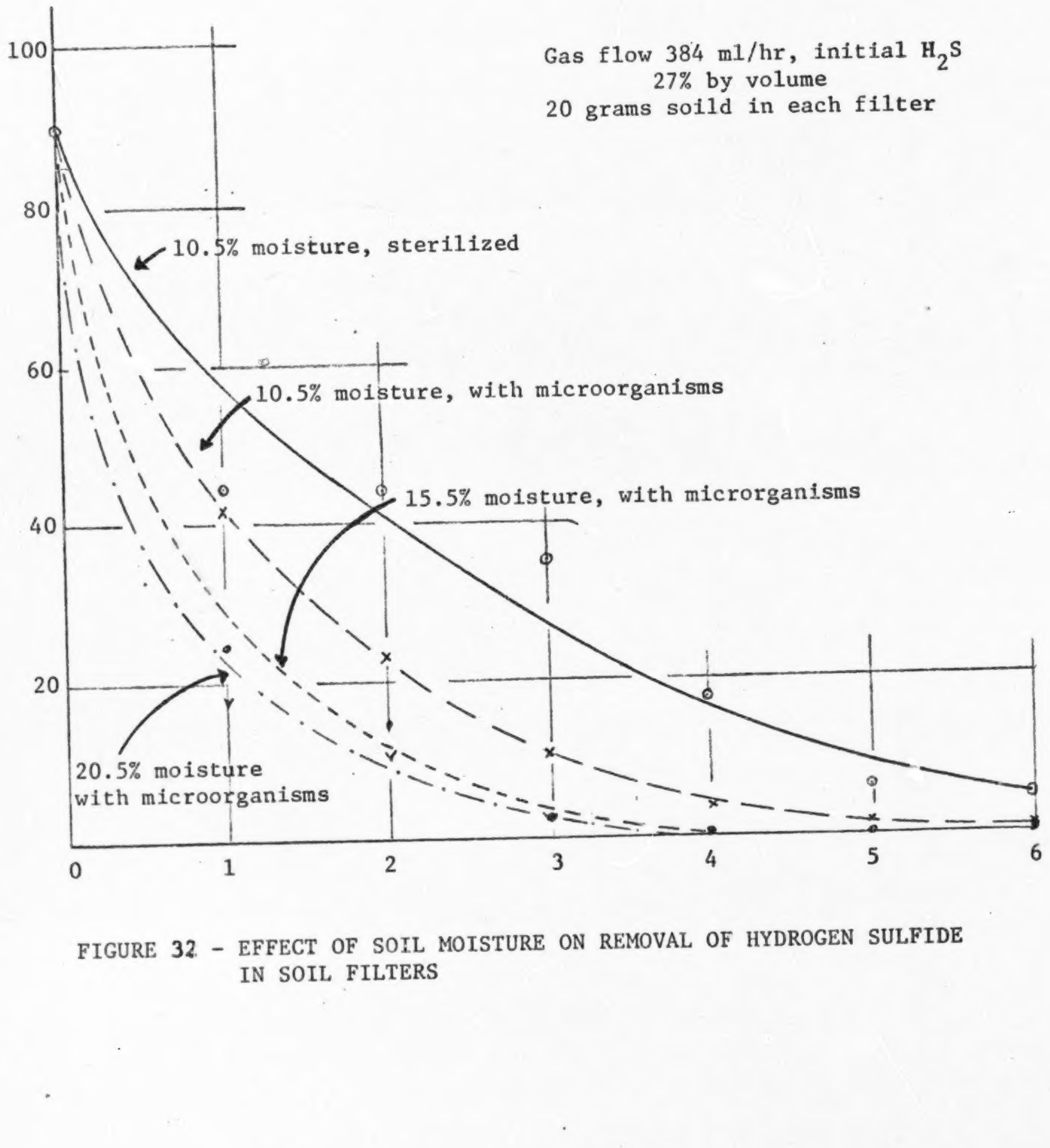


FIGURE 32 - EFFECT OF SOIL MOISTURE ON REMOVAL OF HYDROGEN SULFIDE IN SOIL FILTERS

Test Results with Methyl Mercaptan

Three distinct soils were utilized in a study of the removal capabilities of soil filters with methyl mercaptan. These types were: (1) a fertile loam soil from the University of Washington greenhouse, (2) Norma Fine Sandy Loam - located in Snohomish County, Washington and characteristic of western Washington soils, and (3) Manastash Fine Sandy Loam - a typical eastern Washington soil from Kittitas County.

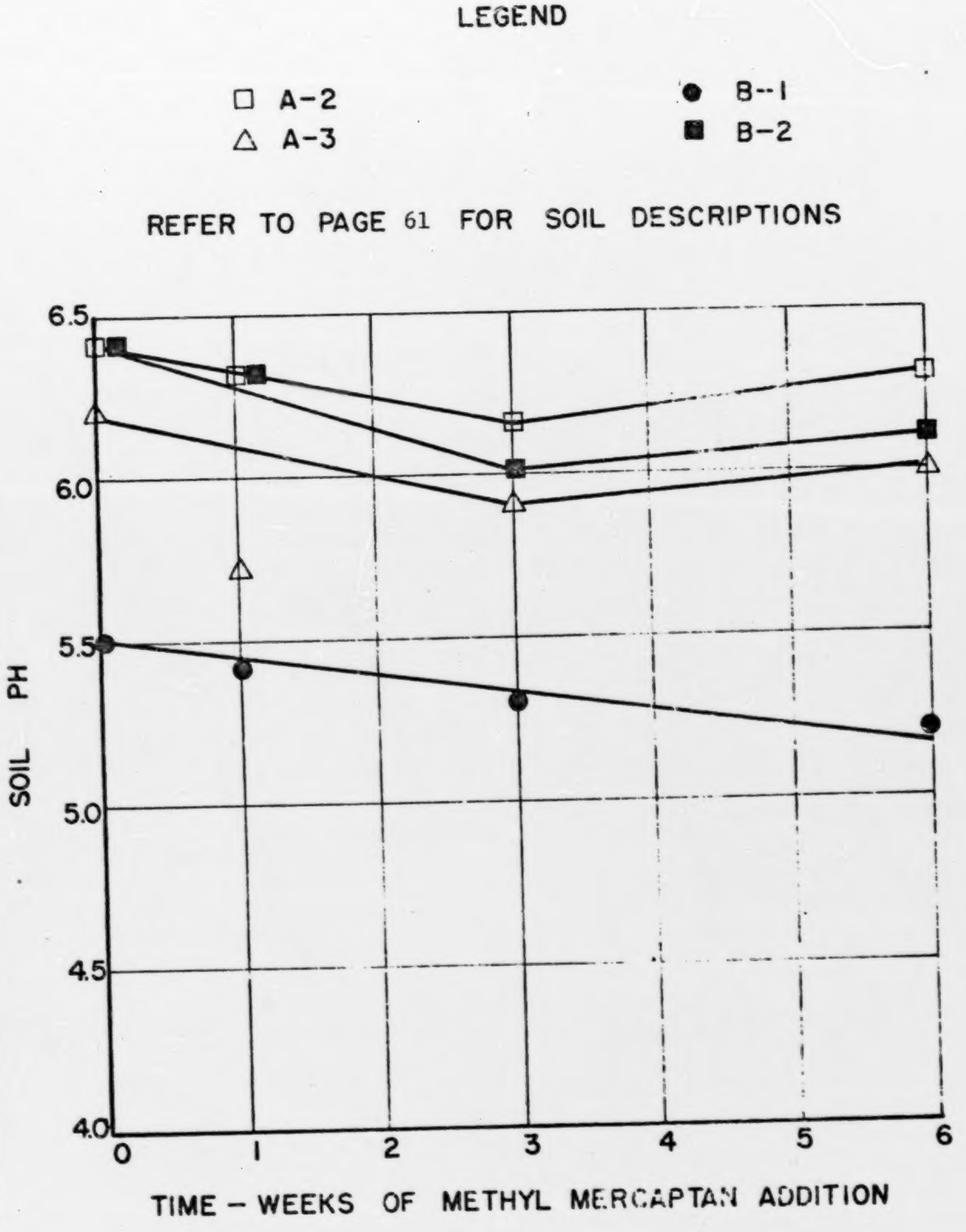
In an attempt to eliminate pH drop, 10.2 grams of KH_2PO_4 and 10.65 grams of Na_2HPO_4 were added to each of a set of three columns, other conditions being identical to another set of three columns. These amounts were governed by the quantity of irrigation water which could be added to each soil column. These additions were necessary since previous research using hydrogen sulfide evidenced a significant drop in elution water pH, and hence soil pH.

Over the first three weeks of the study, the soil pH dropped steadily, followed by an increase over the last three weeks to nearly the original value, as shown in Figure 33. Correspondingly, Figure 34 illustrates that the soil sulfate content increased over the first four weeks and decreased over the latter two, indicating the initial formation of sulfuric acid from the methyl mercaptan followed by its conversion to other compounds. An increase in organic matter occurred in all columns during the course of the study, as seen in Figure 35. This increase is attributed to both an increase in microbial life and to organic sulfur materials deposited by the microbes in the soil. Throughout the six-week research period, the elemental sulfur content of the soil evidenced no noticeable change.

Soil bacteria population was monitored by two separate substrate preparations. Nutrient agar was utilized as an index media for the general soil population present, presumably mainly heterotrophic bacteria. Thiobacillus thiooxidans enrichment media was used as an index media for sulfur oxidizing bacteria (Society of American Bacteriologists, 1957). Figures 36 and 37 indicate the effect of the methyl mercaptan addition upon the bacterial populations, as indicated by these two substrate preparations. Colonies grown on both media showed a decrease throughout the first week of methyl mercaptan

TABLE XI: SOIL COLUMN DESIGNATIONS

Designation	Column Condition
A-1	modified Alderwood Sandy Loam; unbuffered
A-2	Norma Fine Sandy Loam; unbuffered
A-3	Manatash Fine Sandy Loam; unbuffered
B-1	modified Alderwood Sandy Loam; buffering chemicals added
B-2	Norma Fine Sandy Loam; buffering chemicals added
B-3	Manatash Fine Sandy Loam; buffering chemicals added
C	modified Alderwood Sandy Loam; unbuffered; two feet of soil below gas input



REFER TO PAGE 61 FOR SOIL DESCRIPTIONS

FIG. 33 SOIL PH VS TIME (38" LEVEL)

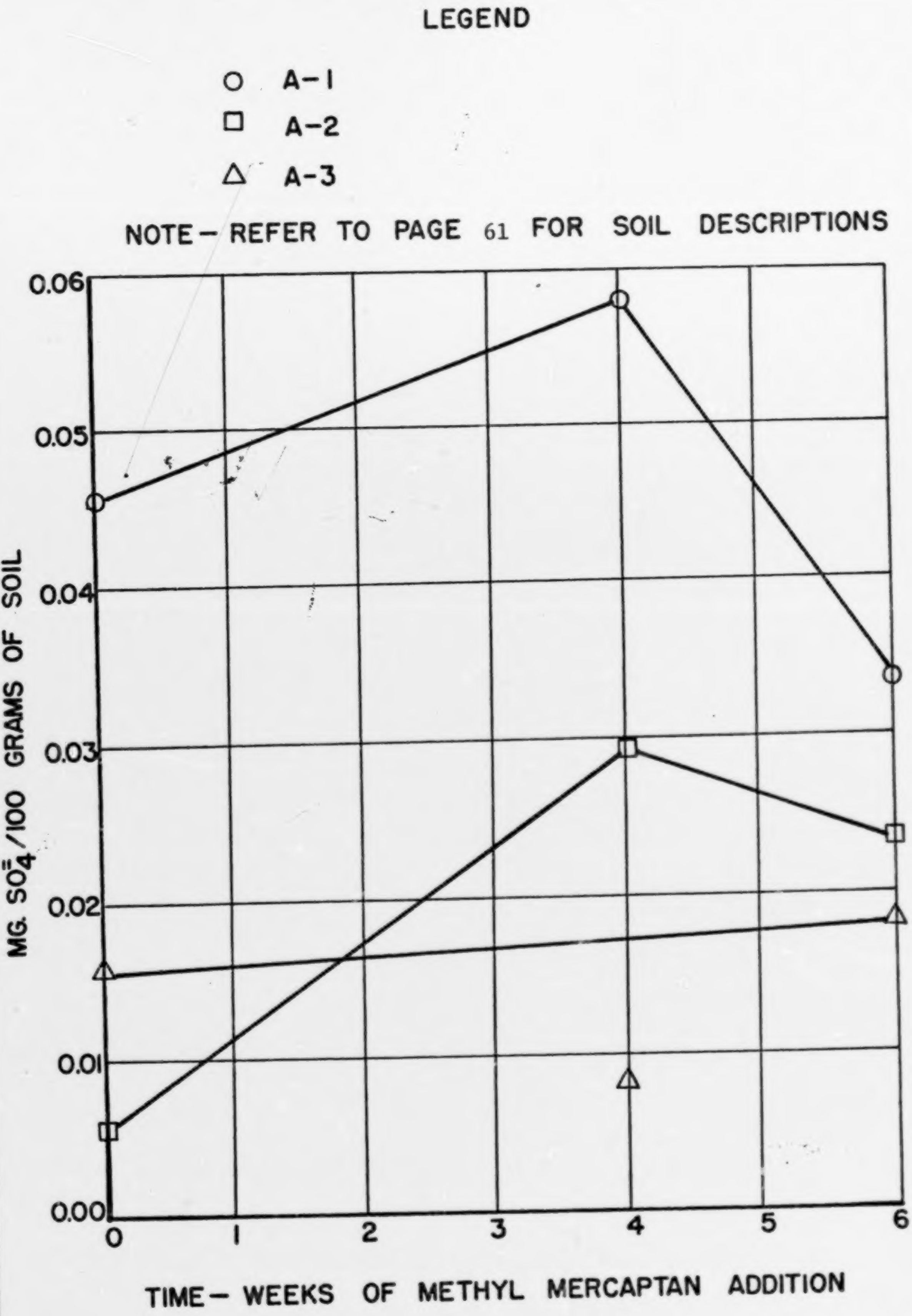


FIG. 34 - SOIL SULFATE (24" LEVEL)

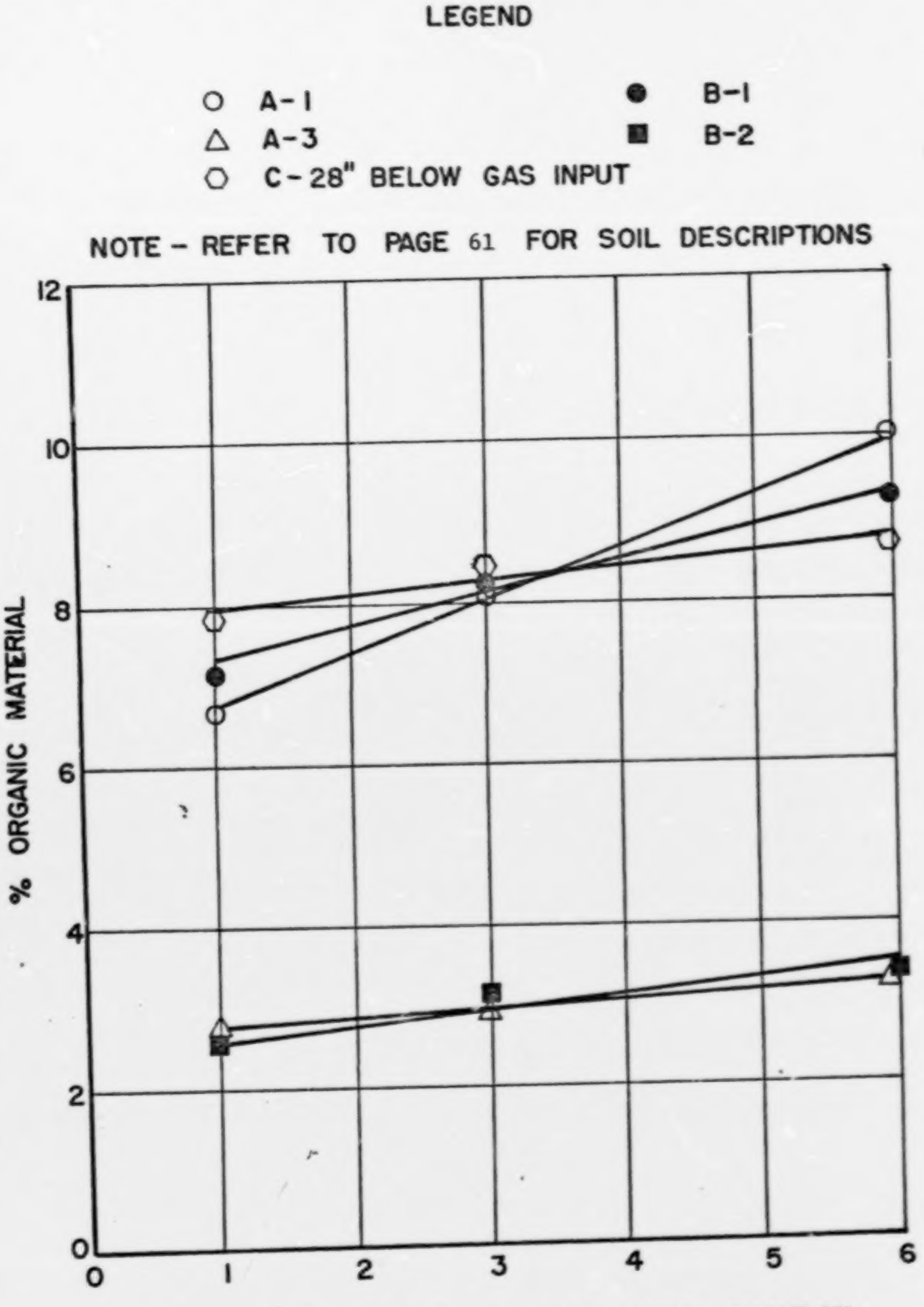
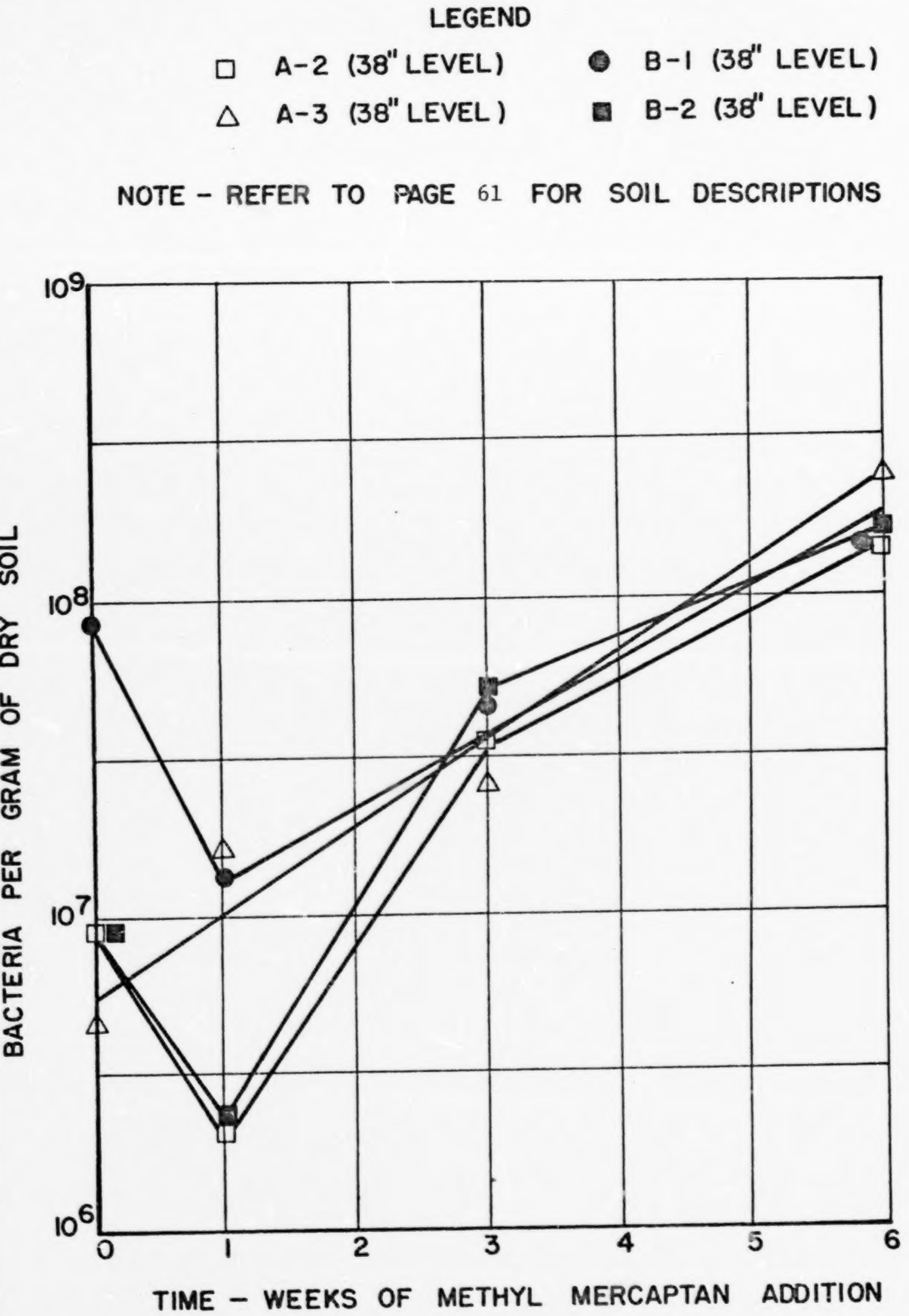
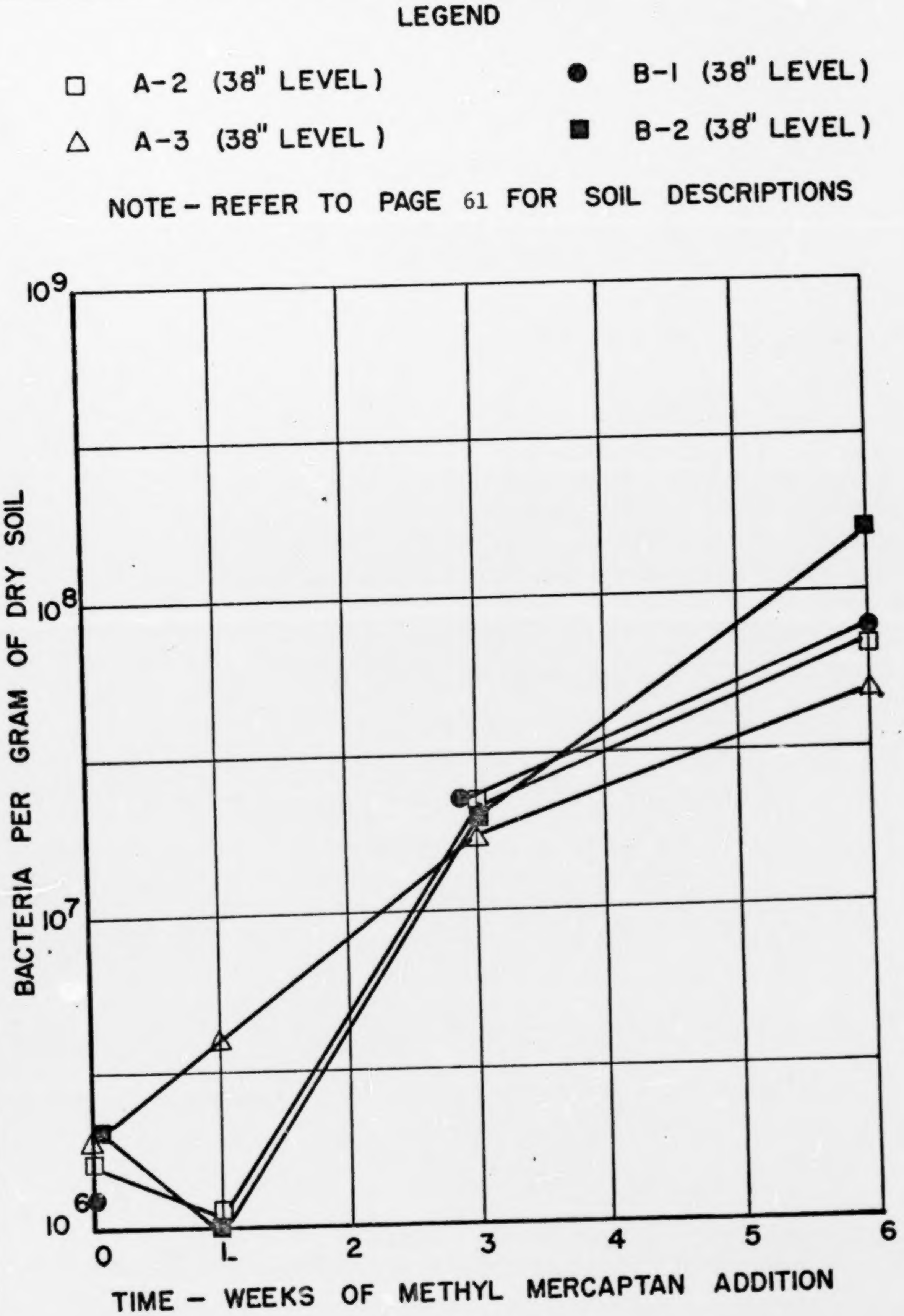


FIG. 35 - SOIL ORGANIC MATERIAL (38" LEVEL)



NOTE - REFER TO PAGE 61 FOR SOIL DESCRIPTIONS

FIG. 36 — BACTERIA COUNTS - NUTRIENT AGAR



NOTE - REFER TO PAGE 61 FOR SOIL DESCRIPTIONS

FIG. 37 - BACTERIA COUNTS - THIOSULFATE AGAR

addition, and then steady increases for the remaining five weeks. These curves indicate the toxicity of methyl mercaptan to many of the bacteria initially present and the growth pattern of those bacteria which were able to utilize methyl mercaptan as a substrate.

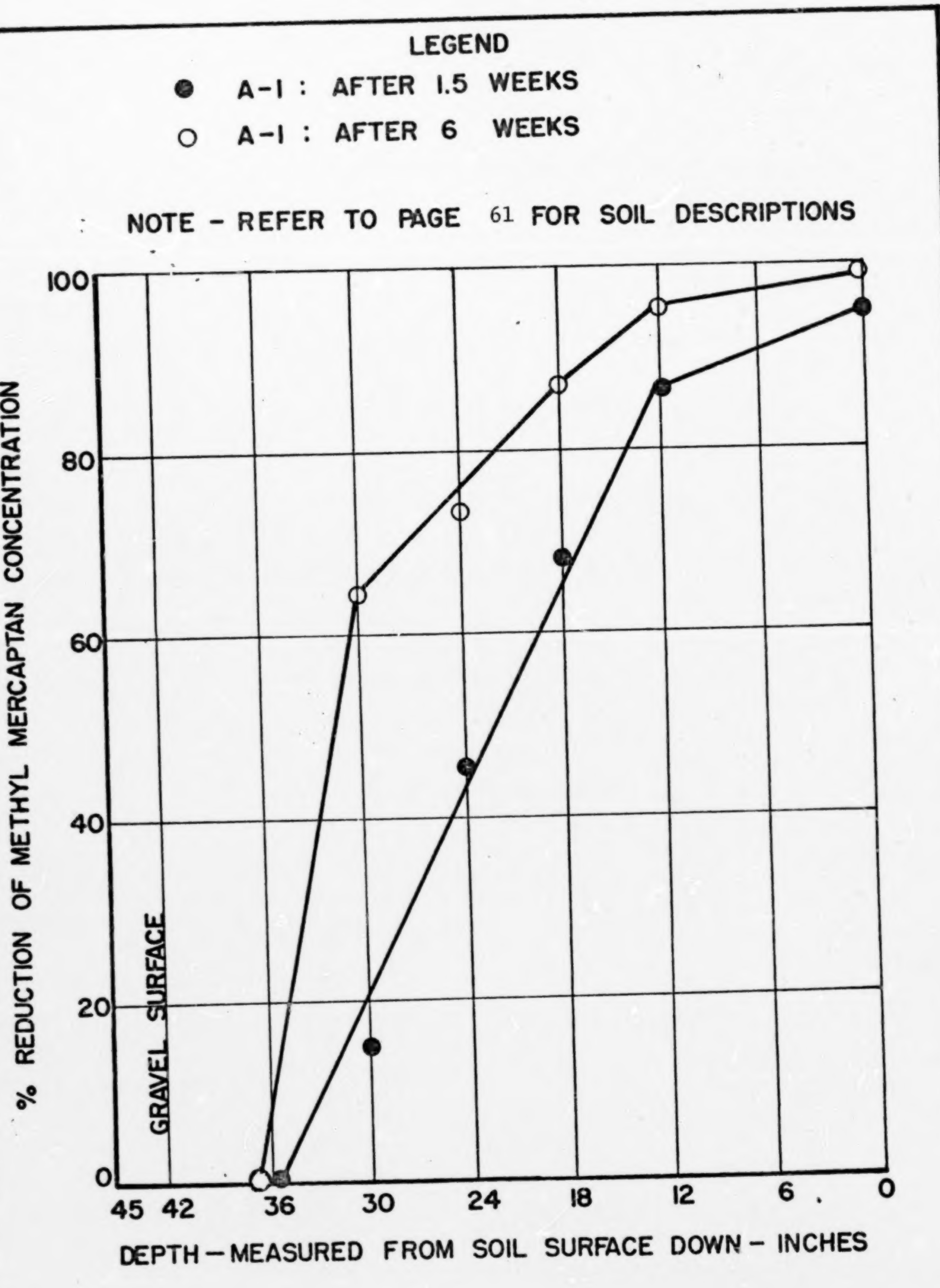
Identification of soil bacteria which were responsible for the degradation was attempted by isolation of pure cultures from the nutrient agar pour plates. Identification of 15 pure cultures produced the following results: 8 Pseudomonas, 2 Bacillus, 2 Nocardia, 1 Flavobacterium, 1 Micrococcus, and 1 Rhizobium. This research did not determine which of these may have been the responsible bacteria or whether several were operating synergistically to accomplish the degradation.

During the course of this research, methyl mercaptan degradation increased from 95% at 1.5 weeks to nearly 100% at the termination. These results, shown in Figure 38, indicate two important considerations. First, the removal efficiency increased as the research progressed. This occurred simultaneously with a bacterial population which was still increasing at the study termination, indicating that the full potential of the system had not been reached after six weeks. Second, installations may be constructed using 3-1/2 feet of soil or less for the practical removal of methyl mercaptan from streams of air.

At the 95% removal rate the methyl mercaptan flow rate was 3200 ppm, whereas at the 100% removal rate the methyl mercaptan flow rate was 775 ppm. This indicated attainable degradation rates between 0.85 and 2.68 liters S.T.P. of methyl mercaptan/week/cubic foot of soil.

The back pressure of the seven soil columns combined was not found to be excessive. At a total mixture flow of 320 ml/minute, the back pressure was measured to be 1.1 inches of water.

One soil column was constructed with two feet of soil beneath the gravel layer, but identical to the other columns in all respects. This column indicated no methyl mercaptan settlement or diffusion more than six inches below the gravel layer. In addition, no increase in the bacteria population occurred on either media at a depth 22 inches below the gravel layer. Thus, in this study, the soil at elevations below input depth did not appear to be useful in mercaptan degradation and therefore trench excavation below the discharge pipe and gravel distribution zone is not necessary for facilitation of biological decomposition of methyl mercaptan.



NOTE - REFER TO PAGE 61 FOR SOIL DESCRIPTIONS

FIG. 38— CUMULATIVE MERCAPTAN REDUCTION VS. SOIL DEPTH

REMOVAL RESULTS WITH METHANE

Several series of soil filter tests were run with methane either as the sole gas constituent or mixed with other gases. In all the tests, methane gas was not removed by the soil system. Thus, this one non-polar gas tested shows significantly different travel effects in soil than do the polar gases.

Gas mixtures included methane and air; air, methane and hydrogen sulfide; methane, hydrogen sulfide and carbon dioxide enriched air. The highest methane concentration reduction was 5.9%; the lowest, 0%. These removal values are within the limits of error of the gas chromatograph used for analyses so that no methane removal can be attributed to the soil system.

SUMMARY AND CONCLUSIONS

1. The soil filter offers a reasonable mechanism for removing polar gases such as hydrogen sulfide and methane mercaptan from air streams.

2. At high concentrations of hydrogen sulfide, above 100 mg/l, the biological removal mechanisms are not significantly operative in the removal of gases in soil filters and chemical mechanisms appear to provide the means for removal. In dry sterile soil, adsorption appears to be the major mechanism together with surface catalysis reactions. In wet soils, removal depends also on the rate of hydrogen sulfide solution in water. At the high hydrogen sulfide concentrations soil service time for removal decreased with increasing moisture content. Thus, at high H_2S loads, the columns should be kept dry.

3. The total reaction at high H_2S concentrations in dry soils appears to be a combination of sulfidation followed by oxidation.

4. A suggested method of design optimization of soil filters for high concentrations of H_2S is based on detention time, reaction temperature, amount and concentration of hydrogen sulfide entering, and the total flow rate. Figure 17 indicates for a given concentration and influent gas temperature, the total flow rate at which the maximum removal of H_2S per unit of time will be obtained.

5. For low concentrations of gas (under 100 mg/l for H_2S), biological systems can operated effectively in moist soil systems. At 775 mg/l methyl mercaptan, moist loam soil had the ability to remove 100% of the methyl mercaptan in quantities of 0.85 liter STP per week per cubic foot of soil. Removal increases with increasing moisture in the range of 5 to 20% moisture.

6. Methane, a representative non-polar gas was not removed in soil columns either singly or in combination with other gases such as air, carbon dioxide or hydrogen sulfide.

7. The soil filter can be operated over long periods of time at gas concentrations which allow microorganisms to operate in the removal process. The system can last for years.

8. At high gas concentrations where microorganisms can not tolerate the gas toxicity, the soil system still has rejuvenation capacity but the sulfidation-oxidation process is gradually reduced in removal effectiveness.

9. Proper design based on pilot studies and care in providing proper mechanisms for removal will make the soil filter an effective tool for control of malodorous gases.

APPENDIX A: MICROBIAL POPULATIONS INHABITING SOIL FILTERS

R. G. Benedict and D. A. Carlson

The populations of microorganisms which inhabit the soil are numerous; the varieties of these organisms which can tolerate various concentrations of toxic gases,such as hydrogen sulfide, when the gas is injected into the soil environment, are not documented. Genera and species likely to be involved in the oxidation of hydrogen sulfide alone or in symbiotic combination has not been established. Nevertheless, soil microorganisms play an active role in the stabilization of injected polar gases. It was the concern of this phase of the project to determine in a preliminary fashion, which aerobic and facultative organisms could exist in soil filters subjected to hydrogen sulfide injection.

Microfloral changes in soil columns subjected to metered amounts of hydrogen sulfide were studied over periods of two and four weeks. Plating media were chosen to provide for aerobic heterotrophic types and certain facultative autotrophic microorganisms within the columns.

Difco nutrient agar at pH 6.8 was used as a plating substrate for heterotrophic microorganisms capable of initiating growth near neutrality. Gram positive sporeformers such as Bacillus sp., gram negative rods, Pseudomonas, Escherichia, Proteus, Serratia and others, and some cocci could be expected to grow. The rather low C:N ratio of this medium would not encourage the development of the lower fungi and total counts of these forms were expected to be low in the test soil used.

Non - aciduric autotrophic sulfur oxidizers growing near neutral pH should be able to grow on enrichment medium suitable for Thiobacillus thioparus isolation. The media recommended by Vishniac and Santer (1957) consists of sodium thiosulfate, basal medium and trace mineral stock. The ingredients include the following:

MEDIA	
$Na_2S_2O_3\cdot5H_2O$	10 gms
KH_2PO_4	4 gms
K_2HPO_4	4 gms
$MgSO_4\cdot7H_2O$	0.8 gms
NH_4Cl	0.4 gms
Trace Mineral Sol'n	10 ml
H_2O	1000 ml
pH was 6.9	

TRACE MINERAL SOLUTION	
E D T A	50 gms
$ZnSO_4\cdot7H_2O$	22 gms
$CaCl_2$	5.54 gms
$MnCl_2\cdot4H_2O$	5.06 gms
$FeSO_4\cdot7H_2O$	4.99 gms
$(NH_4)_6Mo_7O_{24}\cdot4H_2O$	1.10 gms
$CuSO_4\cdot5H_2O$	1.57 gms
$CoCl_2\cdot6H_2O$	1.61 gms
H_2O	1000 ml
Adjust pH to 6.0 with 20% KOH	

(Note: The $Na_2S_2O_3\cdot5H_2O$ is dissolved in sterile water and added to the basal medium after the agar and basal media have been separately sterilized. Ten grams of $Na_2S_2O_3.5H_2O$ dissolved in 13 ml distilled water with a resultant volume of 18.2 ml. This procedure avoids decomposition of the $Na_2S_2O_3$ which occurs readily above 100°C.)

Plates for the study of actinomycetes were prepared according to Benedict et al's (1955) modification of Lindenbein's media (1952) wherein L + arginine replaces glycine as the sole source of nitrogen to provide an amino acid more easily utilized by many species of *Streptomyces*. The media ingredients are as follows:

glycerol	2%	by volume
L + arginine - HCl	0.25%	
NaCl	0.1 %	
K_2HPO_4	0.1 %	
$FeSO_4$	0.01%	
$MgSO_4.7H_2O$	0.01%	
$CaCO_3$	trace	
Agar	2%	

pH adjusted to 6.8 - 7.0

Benedict et al (1957) conducted viable cell counts on *Serratia marcescens* and found that as much as 0.3 ml of diluent plus cells could be spread on well tempered dry plates with "Z" shaped streak rods fashioned from 2 mm diameter glass tubing approximately eight inches long.

Three soil columns were packed with a fertile loam obtained from the Drug Plant Gardens of the College of Pharmacy, University of Washington, December 21, 1968. The soil had been exposed to excess moisture in outside storage at temperatures of 30 - 45°F prior to packing of the columns. Samples from the soil indicated an initial count of about 2.5×10^6 thiosulfate oxidizers and 11.4×10^6 heterotrophs per gram of dry soil. The average soil moisture was 416 mg water / gram of wet soil.

In a rough approximation of the different types of microbes on the nutrient agar, the normal flora contained about 48 bacterial colonies of which seven belonged to *Bacillus* sp. There were, in addition, 16 actinomycetes and one mold.

The three filter columns flow rates were respectively 600 ml /min (column W) 100 ml/min (column A) and 100 ml/min (column C control). Gas streams to columns A and W contained 100 mg/ 1 hydrogen sulfide in air. Column C received only air. The columns were six inches in diameter and 22 inches high with rauschig rings two inches deep in the base of each column as a gas distribution area. For the control filter and the filter receiving 100 ml/min of H_2S - air, sampling ports were located at three inches and 13 inches from the top of the column. In the filter receiving 600 ml/min of H_2S - air, the sampling port location was 9 1/2 inches from the top.

Soil samples for bacteriological analyses were collected in small sterile plastic petri dishes. Sufficient wet soil was taken so that approximately one gram dry soil would be available. Samples were taken one and two weeks after initiation of gas flow to the columns. The approximate distribution of organisms found in the soil filters is shown in Table A-I for growth on nutrient agar (which includes heterotrophic and facultative H_2S oxidizers capable of initiating growth on nutrient agar) and on Vishniac-Santer thiosulfate agar. Macroscopic examination of the various types of bacterial colonies on the thiosulfate plates revealed that the colonies ranged from 0.1 to 2.5 mm in diameter and, microscopically speaking, consisted almost entirely of tiny cocco bacilli at the lower size limit (0.5 X 1μ) given for the genus, Thiobacillus. According to Skerman (1967), the nine species of Thiobacillus now recorded consist of five strict autotrophs and three facultative autotrophs. The latter give copious growth on nutrient agar.

Aeration only in the control column C at 35°C raised the viable heterotroph counts at two weeks. Column A, with the same flow rate but including 100 mg/l H_2S, also showed increased heterotrophic growth at the upper port, three inches from top of the column, at both 1 and 2 weeks after initation of gas flow. The lower port, nearer the gas input zone, showed a decreased count at one week but an increase to greater than the inital count at the second week. Counts of heterotrophs in the center sampling port of column W, receiving a flow rate of 600 ml/min containing 100 mg/l H_2S, decreased from 11 X 10^6 to 7 X 10^6/gm of dry soil after one week but thereafter increased significantly to 33 X 10^6/gram of dry soil. These data show that heterotrophs readily survive in concentrations of 100 mg/l H_2S.

Viable counts of strict and facultative autotrophs showed more sensitivity to H_2S than did the heterotrophs. They also revealed a necessity for moisture as shown by a decrease in counts in the lower portion of column A which dried out during the test period. The moisture content change in the lower portion of column A was from 33% to 12% moisture. The proportionately greater drop at one week in counts of autotrophs, compared to the heterotrophs, also may be a reflection of the higher 35°C incubation temperature somewhat above the optimum for some of these microorganisms.

Actinomycetes, as a group, were quite prominent under the conditions of testing. Most of these appeared to be Streptomyces but some were probably Nocardia sp. The actinomycetes averaged about 23% of the viable cell population. Levels of Bacillus sp. were quite constant at 8% with strains of B. mycoides, B. subtilis and B. cereus predominating. Pigmented forms such as Serratia, Flavobacterium, Sarcina and Pseudomonas were quite rare as were morphologically distinct forms such as Rhizobium and Arthrobacter.

The strict autotrophs appeared to be mainly species of Thiobacillus. They probably included such species as Th. thioporus and Th. denitrificans (and a few others) but not Th. thiooxidans, Th. concretivorus or Th. ferroxidans all of which require a much lower pH for growth initiation.

Table A-I Approximate Distribution of Types of Microorganisms In Soil Columns after Two Weeks Exposure to H_2S-Air Mixture (Excluding Strict Autotrophs) as Indicated on Nutrient Agar Media.

Column Designation and Port	Column Sampling Port	Actinomycetes	*Bacillus* Sp.	Fungi	Other Heterotrophs	*Pseudomonas fluorescens* Sp.	Colony Count
WM	Center Port 600 ml/min H_2S-air	25%	8%	2%	65%	0	142 289
AL	Lower Port 100 ml/min H_2S-air (dry)	55%	8%	2%	35%	0	187
AH	Upper Port 100 ml/min H_2S-air	24%	17%	0	59%	0	233
CL	Lower Port Control 100 ml/min air	17%	8%	2%	71%	2%	110
CH	Upper Port Control 100 ml/min air	25%	9%	0	62%	4%	112

APPENDIX B: THE SEEPAGE OF A GAS THROUGH ODOR-REDUCTION SOIL BEDS

Bruce W. Hunt

INTRODUCTION

An essential part of the design of odor reduction systems involves the prediction of gas seepage rates from buried, porous pipes under a specified pipe pressure and flow geometry. Consequently, the following study was undertaken in the fall of 1968 in an effort to contribute to an understanding of the fluid mechanics for such a system.

EQUATIONS OF MOTION

The theory of gas seepage through porous media seems to have been formulated first by the Soviet scientist L. S. Leibenzon in 1928. A somewhat different, but equivalent, formulation was published in our Western literature by Muskat (1937). The formulation which will be used in this report is identical to that given by Aravin and Numerov, which in turn is based upon the original work by Leibenzon. (Aravin and Numerov, 1965)

The steady, two-dimensional, isothermal seepage of an ideal gas is governed by the Laplace equation

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0 \qquad (1)$$

in which the potential ϕ is defined as

$$\phi = \left(\frac{k_0 g}{2\mu R T}\right) P^2 \qquad (2)$$

In Eq. 2 the symbol P represents the absolute pressure, k_0 represents the physical or intrinsic permeability of the soil, μ is the dynamic viscosity of the gas, g is the acceleration of gravity, T is the absolute temperature in degrees Rankine, and R is the universal gas constant calculated from the equation

$$R = \frac{1545 \times 32.174}{\text{Molecular Wt. of Gas}} \quad \frac{\text{ft-lb}}{\text{Slug - °Rankine}}$$

The product of the gas weight per unit volume, γ, and the velocities, u and v, in the x and y directions, respectively, are given by

$$\gamma u = - \frac{\partial \phi}{\partial x} \tag{3}$$

and

$$\gamma v = - \frac{\partial \phi}{\partial y} \tag{4}$$

If σ represents the soil porosity, then the discharge velocities u and v are related to the actual seepage velocities by the equations

$$u = \sigma \frac{dx}{dt} \tag{5}$$

$$v = \sigma \frac{dy}{dt} \tag{6}$$

In part of the following work it will be useful to write ϕ as the real part of the analytic function

$$w(z) = \phi\ (x, y) + i\ \psi\ (x, y) \tag{7}$$

Use can be made of the Cauchy-Riemann equations and the relationships between the direction cosines of the unit normal and unit tangent of an arc to show that lines of constant ψ are tangent to streamlines of the flow. Furthermore, it can be shown in a similar way that the difference in ψ between any two streamlines is equal to

$$\psi_2 - \psi_1 = \pm \cdot \dot{m}\ g \tag{8}$$

The symbol $\dot{m}$ in Eq. 8 represents the two-dimensional mass flow rate between the two lines of constant ψ. If the derivative of Eq. 7 is taken, and if Eqs. 3 and 4 are used together with the Cauchy-Riemann equations, it is found that

$$\frac{dw(z)}{dz} = - \gamma\ (u - iv) \tag{9}$$

FLOW SOLUTIONS

Solution for an Infinite Number of Pipes. -- The geometry and boundary conditions which are considered in this section are shown in Figures B-1 and B-2. It is assumed that the row of porous pipes is buried in a horizontal layer of relatively porous material such as gravel. Furthermore, it is assumed that boundaries at the ends of all pipes are vertical and relatively impermeable and that the row of pipes extends to plus and minus infinity in the horizontal direction. Obviously, this last restriction can be removed if any of the vertical streamlines shown in Figure B-1 are replaced by vertical, impermeable boundaries.

The harmonic function ϕ which satisfies the boundary conditions shown in Figures B-1 and B-2 is

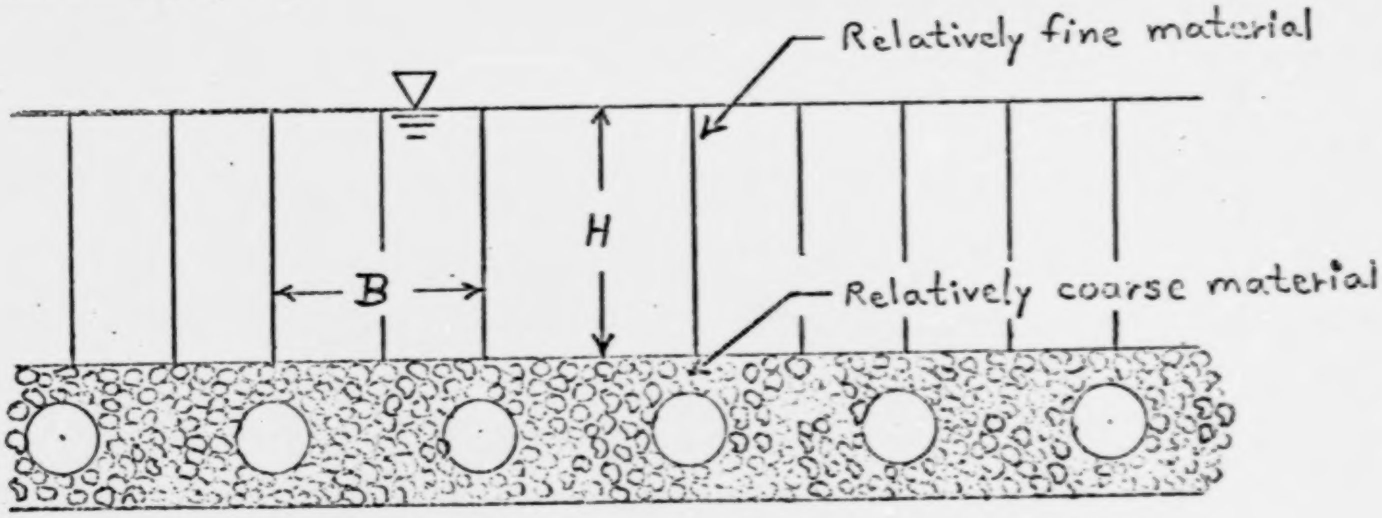


FIG. B-1. - STREAMLINES AND GEOMETRY FOR AN INFINITELY LONG ROW OF POROUS PIPES BURIED A DISTANCE H BENEATH THE GROUND SURFACE.

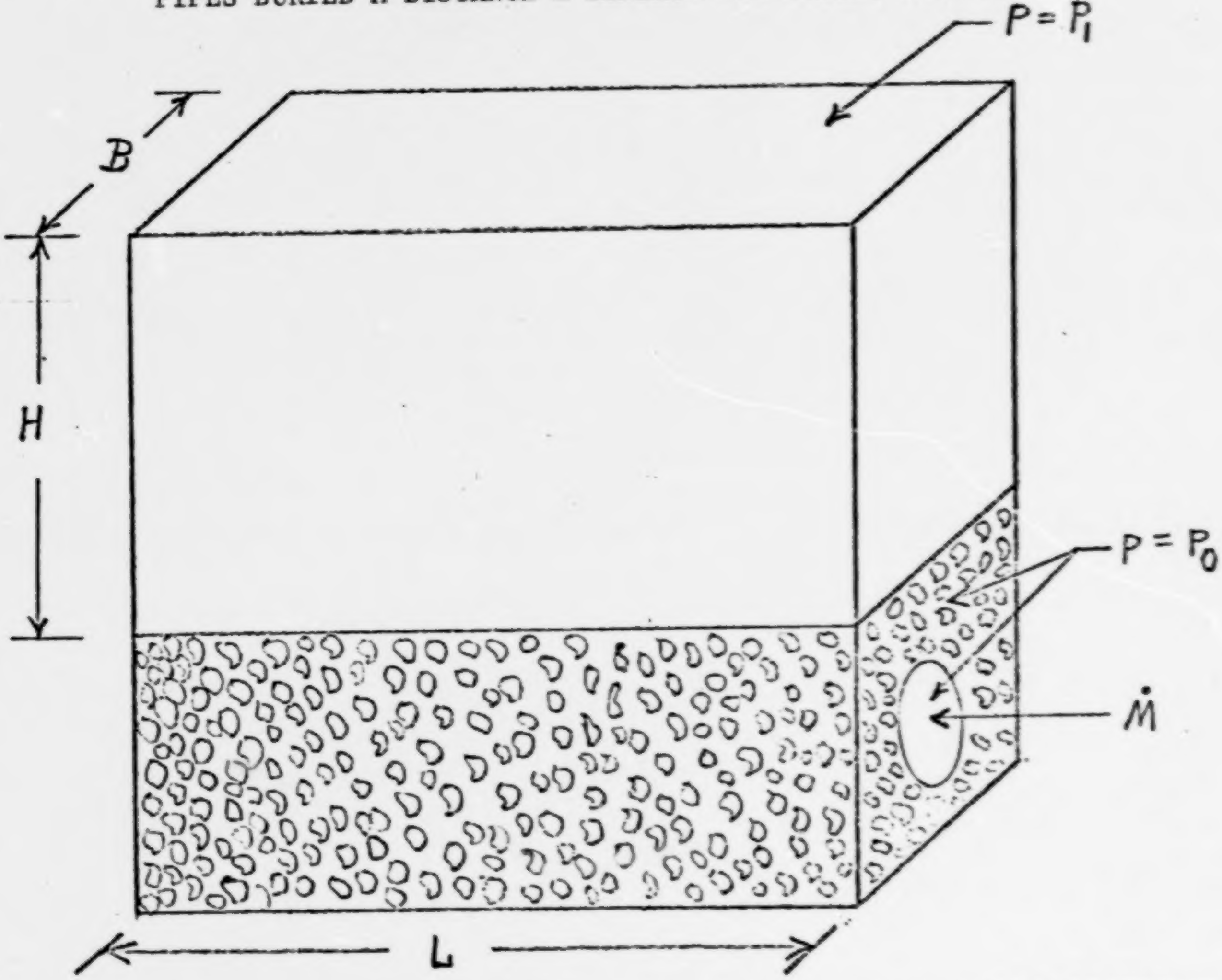


FIG. B-2. - BOUNDARY CONDITIONS FOR ONE OF THE POROUS PIPES SHOWN IN FIG. B-1, WHICH ARE SPACED A DISTANCE B APART.

$$\phi = \frac{k_o g}{2\mu RT} [P_0^2 - (P_0^2 - P_1^2) \frac{y}{H}] \qquad (10)$$

Eq. 10 has previously been given as a solution to this problem by Muskat (1937). From Eqs. 2 and 10 the pressure distribution within the soil is found to be

$$\frac{P}{P} = k - [1 - (\frac{P_1}{P_0})^2] \frac{y}{H} \qquad (11)$$

The vertical velocity v is obtained from Eqs. 4, 10 and 11 together with the ideal gas law as

$$v = \frac{k_0}{2\mu H} \frac{P_0^2 - P_1^2}{P_0^2 - (P_0^2 - P_1^2) \frac{y}{H}} \qquad (12)$$

Therefore, the constant mass efflux past any horizontal cross section in Fig. B-2 is

$$\dot{M} = \frac{k_0 BL}{2\mu HRT} (P_0^2 - P_1^2) \qquad (13)$$

Note that $\dot{M} = \dot{m}L$ is the total mass flow rate leaving a pipe of length L.

The average time for an element of gas to reach the ground surface may be found by integrating Eq. 6. That is,

$$\int_0^{t_1} dt = \sigma \int_o^H \frac{dy}{v} \qquad (14)$$

Substituting Eq. 12 into Eq. 14 and integrating gives the result:

$$t_1 = \frac{4}{3} \frac{\sigma H^2 \mu}{k_0} \frac{P_0^3 - P_1^3}{(P_0^2 - P_1^2)^2} \qquad (15)$$

Eq. 15 shows the potentially useful result that, if all other variables are held constant, the average time required for an element of gas to reach the ground surface varies directly with the square of the depth H at which the pipes are buried.

Another interesting conclusion can be drawn from the inspection of Eqs. 11, 12 and 13. Since gravity is neglected in calculating the flow of a gas, it is possible to find the steady-state pressure, velocity, and mass flow rate at any point beneath the pipes simply by setting $H = -\infty$ in each of these three equations. The result is that $P = P_0$, $v = 0$, and $\dot{M} = 0$ everywhere beneath the horizontal row of pipes shown in Fig. B-1. Hence, after flow has continued for a long enough time to ensure steady-state conditions, the value of $\dot{M}$ in Eq. 13 also represents the total mass flux entering each of the pipes.

Solution for a Single Pipe. -- In this section the solution is obtained for a single pipe buried beneath the ground surface. As shown in Fig. B-3, it is assumed that the pipe is surrounded on all sides by permeable soil. Note that the distance H_* in Fig. B-3 is measured to the pipe centerline, whereas the distance H in Fig. B-1 is measured only to the top of the relatively permeable layer of gravel.

The flow geometry of Fig. B-3 is mapped conformally onto the region between the two concentric circles shown in Fig. B-4 by the transformation.

$$\zeta = \frac{z - i\,(H_* + \quad H_*^2 - r_0^2)}{z - i\,(H_* - \quad H_*^2 - r_0^2)} \qquad (16)$$

The value of r_0' in Fig. B-4 is given by

$$r_0' = \frac{H_*}{r_0} + \quad \left(\frac{H_*}{r_0}\right)^2 - 1 \qquad (17)$$

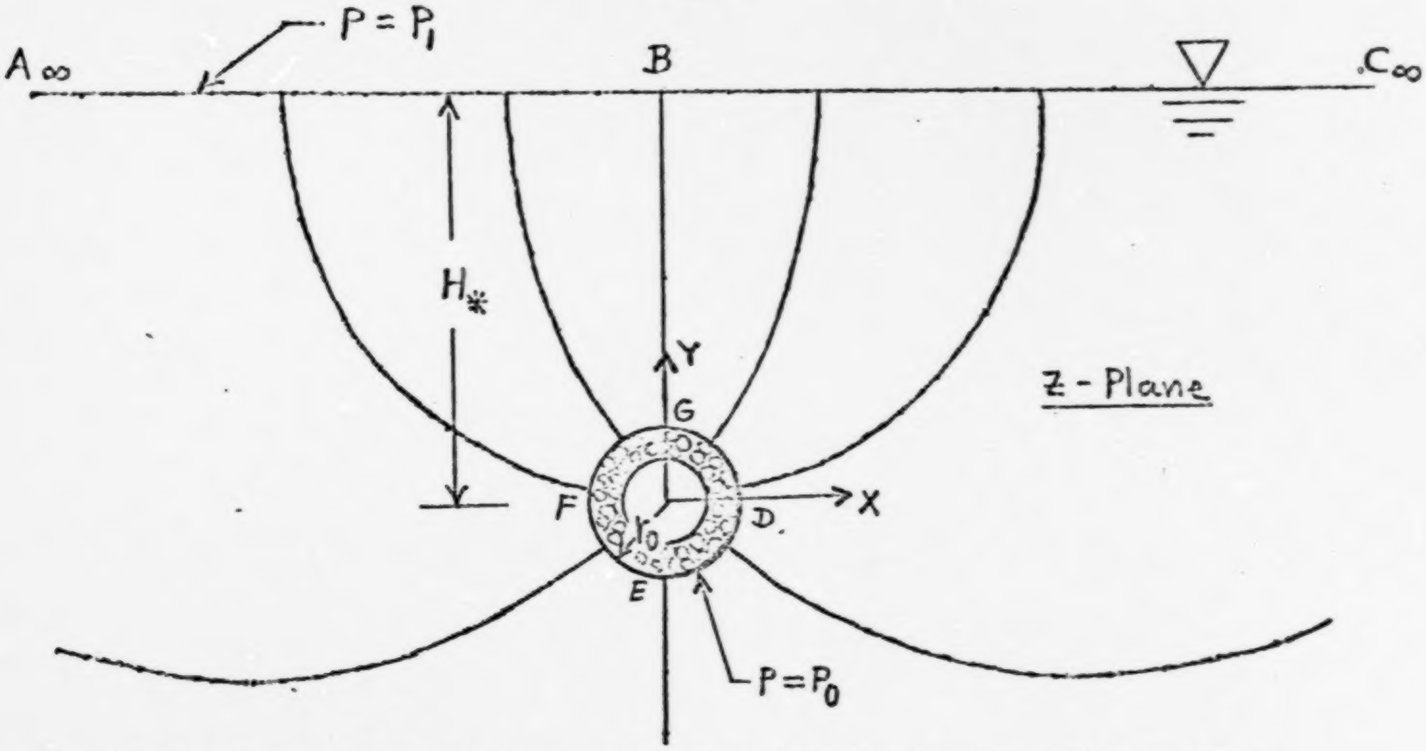

P = P₁
A ∞
B
C ∞
H*
Y
G
Z - Plane
F
r₀
D
X
E
P = P₀

FIG. B-3 - STREAMLINES AND GEOMETRY FOR A SINGLE PIPE BURIED IN A SEMI-INFINITE SOIL BED.

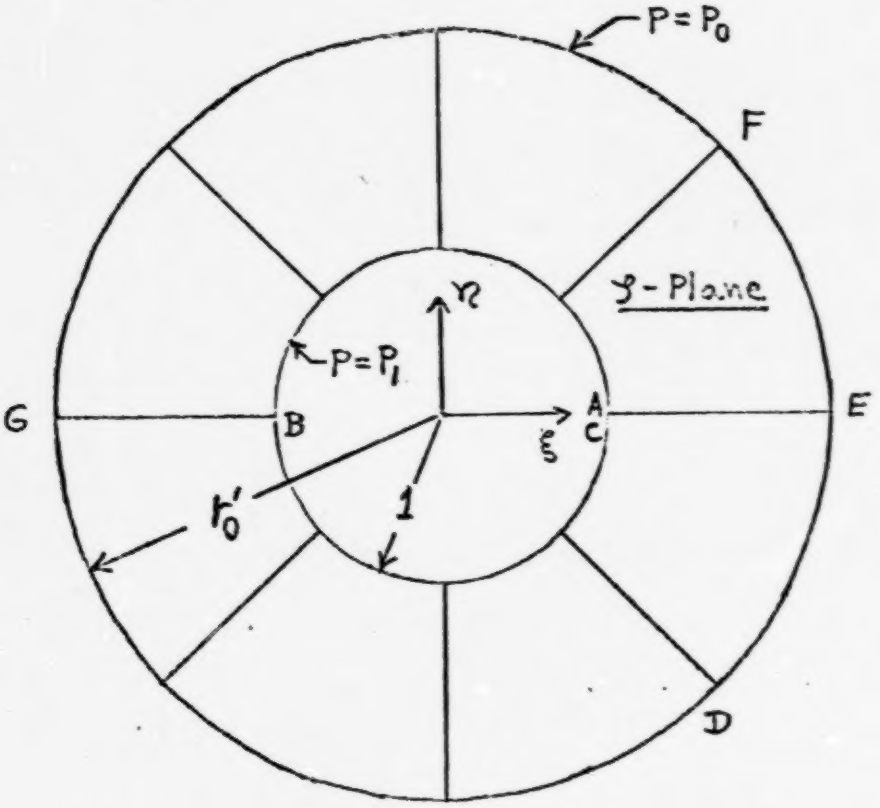

P = P₀
F
η
ζ - Plane
P = P₁
G
B
A
C
ξ
E
r₀'
1
D

FIG. B-4 - THE FLOW GEOMETRY AND STREAMLINES OF FIG. B-3. MAPPED CONFORMALL_ ONTO THE REGION BETWEEN TWO CONCENTRIC CIRCLES.

This transformation can be found in Kober (1957).

The boundary-value problem, after it is transformed by Eq. 16 to the ζ plane, becomes

$$w(\zeta) = \phi\ (\xi,\ \eta) + i\ \psi\ (\xi,\ \eta) \tag{18}$$

$$\operatorname{Re} w\ (\zeta) \Big|_{|\zeta| = 1} = \frac{k_0 g}{2\mu RT} P_1^{\,2} \tag{19}$$

$$\operatorname{Re} w\ (\zeta) \Big|_{|\zeta| = r_0'} = \frac{k_0 g}{2\mu RT} P_0^{\,2} \tag{20}$$

The solution to this elementary problem is the potential for a source at the origin in the ζ - plane:

$$w(\zeta) = \frac{k_0 g}{2\mu RT} \left[\frac{(P_0^{\,2} - P_1^{\,2})}{\ln r_0'} \ln \zeta + P_1^{\,2} \right] \tag{21}$$

The pressure at any point in the physical z - plane of Fig. B-3 may be found by substituting Eqs. 16 and 17 into Eq. 21 and taking the real part of the result. In this manner it is found that

$$\left(\frac{P}{P_0}\right)^2 = \frac{1-\left(\frac{P_1}{P_0}\right)^2}{\ln \frac{H_*}{r_0} + \left(\frac{H_*}{r_0}\right)^2 - 1} \ln \frac{\left(\frac{x}{H_*}\right)^2 + 1 - \frac{y}{H_*} + 1 - \left(\frac{r_0}{H_*}\right)^{2\ \ 2}}{\left(\frac{x}{H_*}\right)^2 + 1 - \frac{y}{H_*} - 1 - \left(\frac{r_0}{H_*}\right)^{\ \ 2}}$$

This transformation can be found in Kober (1957).

The boundary-value problem, after it is transformed by Eq. 16 to the ζ plane, becomes

$$w(\zeta) = \phi\ (\xi, \eta) + i\ \psi\ (\xi, \eta) \tag{18}$$

$$\operatorname{Re} w(\zeta) \Big|_{|\zeta| = 1} = \frac{k_0 g}{2\mu RT} P_1^{\,2} \tag{19}$$

$$\operatorname{Re} w(\zeta) \Big|_{|\zeta| = r_0'} = \frac{k_0 g}{2\mu RT} P_0^{\,2} \tag{20}$$

The solution to this elementary problem is the potential for a source at the origin in the ζ - plane:

$$w(\zeta) = \frac{k_0 g}{2\mu RT} \left[\frac{(P_0^{\,2} - P_1^{\,2})}{\ln r_0'} \ln \zeta + P_1^{\,2} \right] \tag{21}$$

The pressure at any point in the physical z - plane of Fig. B-3 may be found by substituting Eqs. 16 and 17 into Eq. 21 and taking the real part of the result. In this manner it is found that

$$\left(\frac{P}{P_0}\right)^2 = \frac{1-\left(\frac{P_1}{P_0}\right)^2}{\ln\left[\frac{H_*}{r_0} + \sqrt{\left(\frac{H_*}{r_0}\right)^2 - 1}\right]} \ln \sqrt{\frac{\left(\frac{x}{H_*}\right)^2 + \left[1 - \frac{y}{H_*} + \sqrt{1 - \left(\frac{r_0}{H_*}\right)^2}\right]^2}{\left(\frac{x}{H_*}\right)^2 + \left[1 - \frac{y}{H_*} - \sqrt{1 - \left(\frac{r_0}{H_*}\right)^2}\right]^2}}$$

$$+ \left(\frac{P_1}{P_0}\right)^2 \tag{22}$$

Since the mass flow rate between any two streamlines remains invariant under a conformal transformation, Eqs. 8 and 21 can be used to find the mass flux of gas leaving the pipe. Thus, taking the difference in values of the imaginary part of Eq. 21 after one complete circuit is made about $|\zeta| = 1$ gives

$$\dot{M} = \frac{\pi k_0 L}{\mu R T} \frac{P_0^2 - P_1^2}{\ln\left[\frac{H_*}{r_0} + \sqrt{\left(\frac{H_*}{r_0}\right)^2 - 1}\right]} \tag{23}$$

The mass flow rate $\dot{M}$ in Eq. 23 is the total mass flux leaving a pipe of length L (i.e. $\dot{M} = L\dot{m}$).

It is possible to use Eqs. 6, 9, 16, 17 and 21 to obtain in integral form an expression for the average time required for a fluid element to reach the ground surface along the path x = 0.
The resulting expression is

$$t_1 = \frac{\sigma\,\mu\sqrt{\ln f\left(\frac{H_*}{r_0}\right)}}{k_0\sqrt{(P_0^2 - P_1^2)(H_*^2 - r_0^2)}} \int_0^{H_* - r_0} [H_*^2 - r_0^2 - \eta^2] \sqrt{\ln\left[\frac{\sqrt{H_*^2 - r_0^2} + \eta}{\sqrt{H_*^2 - r_0^2} - \eta}\right]} \, d\eta \tag{25}$$

in which

$$f\left(\frac{H_*}{r_0}\right) = \frac{H_*}{r_0} + \sqrt{\left(\frac{H_*}{r_0}\right)^2 - 1} \tag{26}$$

Eq. (25) can be put in a form which is more convenient for numerical computations by making the substitution

$$\xi = \frac{\sqrt{H_*^2 - r_0^2} + \eta}{\sqrt{H_*^2 - r_0^2} - \eta} \tag{27}$$

The end result of this substitution is

$$t_1 = \frac{8\,\sigma\mu\,(H_*^2 - r_0^2)\sqrt{\ln f\left(\frac{H_*}{r_0}\right)}}{k_0\sqrt{P_0^2 - P_1^2}} \int_1^{f\left(\frac{H_*}{r_0}\right)} \frac{\xi\sqrt{\ln\xi}}{(\xi + 1)^4}\,d\xi \tag{28}$$

Obviously, t_1 in Eq. 28 is the minimum time required for an element of gas to reach the ground surface. Eq. 28 was evaluated numerically with Simpson's quadrature formula upon an IBM 7094 computer at the University of Washington. The results are plotted dimensionlessly in Fig. B-5.

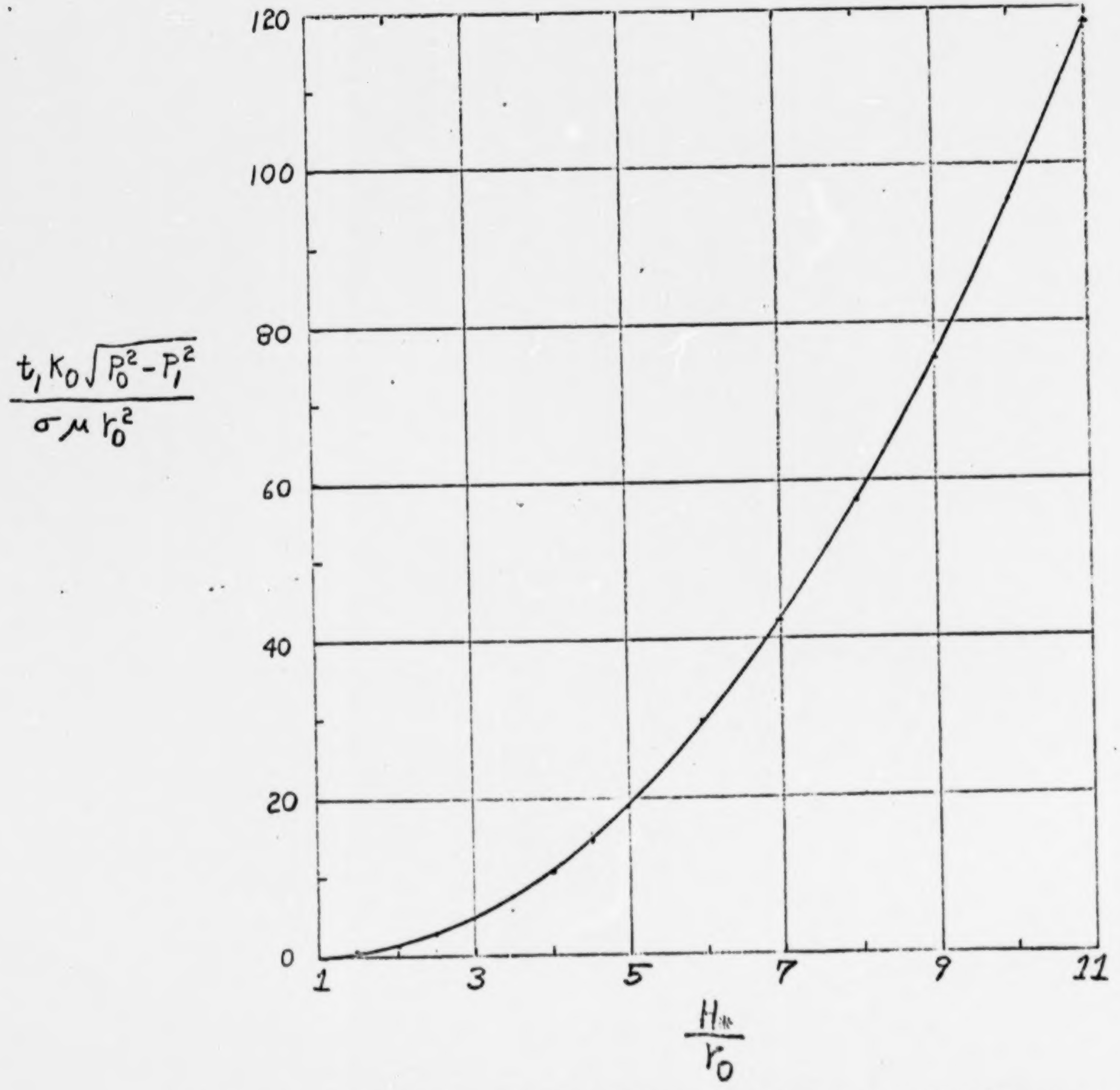


FIG. B-5 - A PLOT OF EQ. 28, WHICH GIVES THE MINIMUM TIME REQUIRED FOR AN ELEMENT OF GAS TO REACH THE GROUND SURFACE IN FIG. 3

EXPERIMENTAL VERIFICATION

A limited number of experimental measurements were made by the author in the Harris Hydraulics Laboratory at the University of Washington. The object of these experiments was to prove the validity of three assumptions which are made in the derivation of Eqs. 1 and 2. These assumptions are (1) that flow within the porous medium can be modeled mathematically by a continuum, (2) that Darcy's law is valid, and (3) that gas expansion within the porous medium can be approximated by the isothermal flow of an ideal gas. Assumptions (1) and (2) have been shown to hold by numerous investigators concerned with the flow of water and heavy fluids through porous media. However, experimental verification of these assumptions for the flow of a gas does not seem to be so prevalent in the literature of fluid mechanics.

A permeameter was constructed by filling a 2.15 inch diameter plastic pipe with 40 inches of 200 micron diameter glass beads. The beads were held in place with porous sand filters, which were placed in each end of the tube. One end of the tube opened to the atmosphere, while the other end was sealed to form a plenum chamber. Mass flow rates entering the plenum chamber were measured with the aid of a Dwyer flow meter, and pressures within the permeameter were measured with a mercury-filled u-tube which was connected to six piezometer taps along the side of the pipe. A schematic drawing of the permeameter is shown in Fig B-6.

Dimensionless pressures along the permeameter are plotted in Fig. B-7 for three separate plenum chamber pressures. The solid line shows the pressure distribution as calculated from Eq. 11. and the experimental values are shown as solid dots. It is observed that experimental and theoretical values agree satisfactorily. Hence, it seems logical to conclude that other details of the flow - such as the travel times given by Eqs. 15 and 28 - are predicted reasonably well by the theory which is used in this report.

The coefficients of permeability for nine separate runs are plotted in Fig B-8 as a function of a Reynolds number (based upon the diameter of the glass spheres). If the flow followed Darcy's law, k_0 would be independent of the Reynolds number and would plot as a horizontal line in Fig. B-8. It is seen from Fig. 8 that k_0 is essentially constant for most of the experimental runs. However, the value of k_0 which was measured for the lowest Reynolds number is about 11 percent below the average value of k_0 for the remaining eight runs. Since Darcy's law is known to hold most closely for flows with low Reynolds numbers, the author is tempted to conclude that this deviation is probably the result of experimental error in measuring the pressures and flow rate for that one run. Experimental measurements by other investigators tend to show that Darcy's law is not followed for Reynolds numbers greater than about 12 (Harr, 1962).

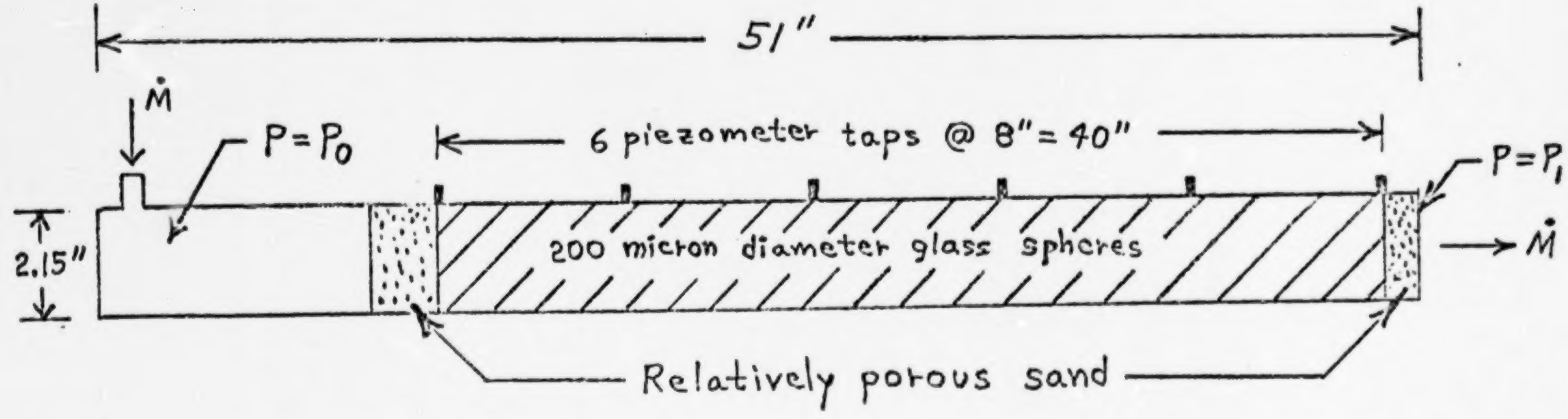

51"
$\dot{M}$
$P=P_0$
6 piezometer taps @ 8" = 40"
$P=P_1$
2.15"
200 micron diameter glass spheres
$\dot{M}$
Relatively porous sand

FIG. B-6 - A SCHEMATIC DRAWING OF THE EXPERIMENTAL PERMEAMETER WHICH WAS USED FOR THIS INVESTIGATION

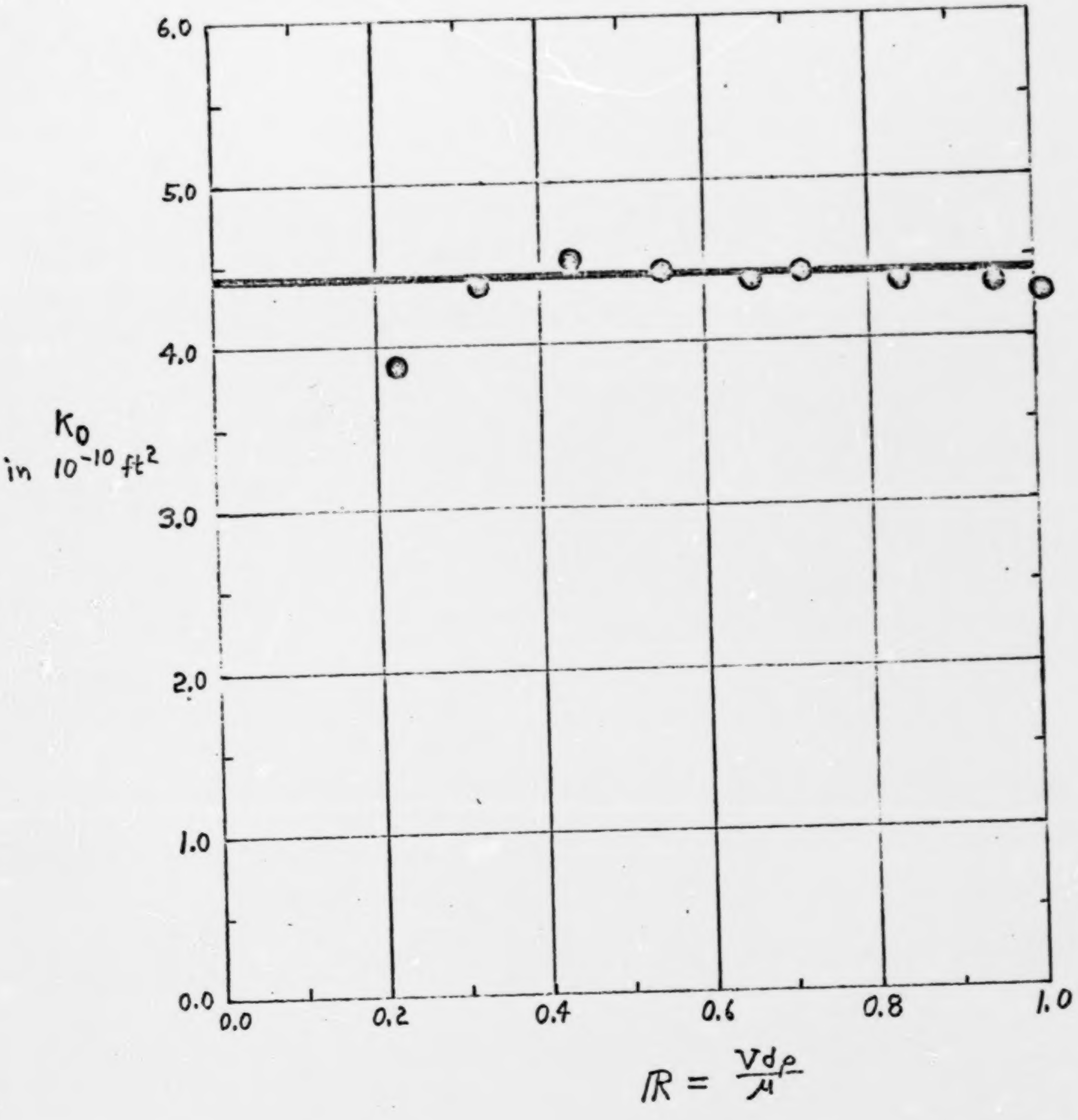


FIG. B-8 - PERMEABILITY COEFFICIENTS MEASURED WITH THE PERMEAMETER SHOWN IN FIG. B-6

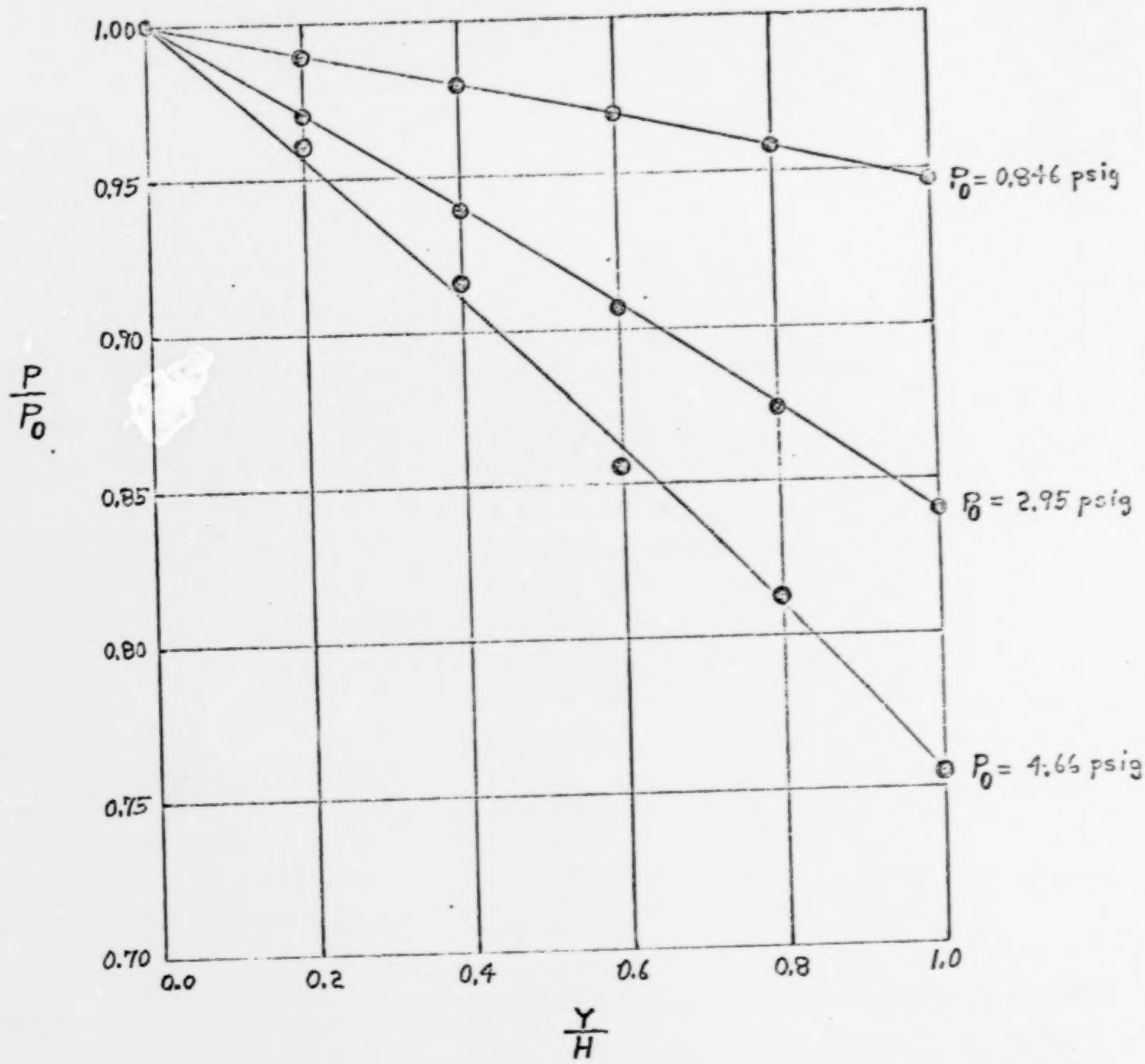


FIG. B-7 - THEORETICAL AND EXPERIMENTAL PRESSURES FOR THE PERMEAMETER SHOWN IN FIG. B-6

SOIL PERMEABILITIES

The only experimental constant which appears throughout this entire analysis is the physical or intrinsic permeability k_0. It is known from previous experimental work (carried out, for the most part, with water) that k_0 depends upon variables such as the soil void ratio, soil structure, soil grain shape, and soil grain size. Hence, k_0 can be expected to vary greatly from soil to soil, so that it must be determined experimentally for each and every separate application of the formulae given in this report. This experimental determination of k_0 is a routine procedure in modern soil-testing laboratories.

Probably the most important practical difference between determining k_0 for a gas and for a heavy liquid is that k_0 for a gas will depend upon the additional variable of soil moisture content. Preliminary work upon determining the effect of soil moisture content upon the air permeability of compacted, cohesive soils has already been done by Langfelder, Chen, and Juntice (1968). These investigators have found for the soils which they tested that k_0 remained virtually unaffected by increasing moisture content until the optimum moisture content was approached. However, near the optimum moisture content the value of k_0 decreased extremely rapidly, and the end result was that the soil became relatively impermeable at that point. It would seem logical to expect this same type of behavior for cohesionless soils as well, although more experimental work should be done in this area before any definite conclusions can be made. If future experimental work shows that this behavior is indeed characteristic of most soils, then it would follow that the moisture content of soil beds used for odor reduction purposes should always be kept below the optimum value.

APPLICATION OF THE THEORY

In practice it will be found that the infinitely long row of porous pipes shown in Fig B-1 will be replaced by a finite number of pipes, such as the system shown in Fig B-9. If the streamlines in Figs. B-1, B-3, and B-9 are compared[1], it is seen that flow conditions between the end pipes can be approximated fairly closely by the results obtained for an infinite row of pipes. Likewise, flow conditions near the two end pipes can be approximated closely by the results obtained for a single pipe, such as the one shown in Fig. B-3. More specifically, if $\dot{M}_{13}$ and $\dot{M}_{23}$ represent mass flow rate given by Eqs 13 and 23, respectively, then the total flow rate in Fig. B-9 is approximately

$$\dot{M}_{total} = 4\,\dot{M}_{13} + \dot{M}_{23} \qquad (29)$$

More generally, if there are N. pipes in a row, then the mass flow rate is given approximately by

$$\dot{M}_{total} = (N - 1)\,\dot{M}_{13} + \dot{M}_{23} \qquad (30)$$

Eq. 30 will hold most closely either for $N = 1$ or for large N. However, it is the author's opinion that the degree of approximation for intermediate values of N will also be good.

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[1] The streamline patterns in Figs. B-3 and B-9 were determined by the author with an electrical analogy apparatus at the University of Washington.

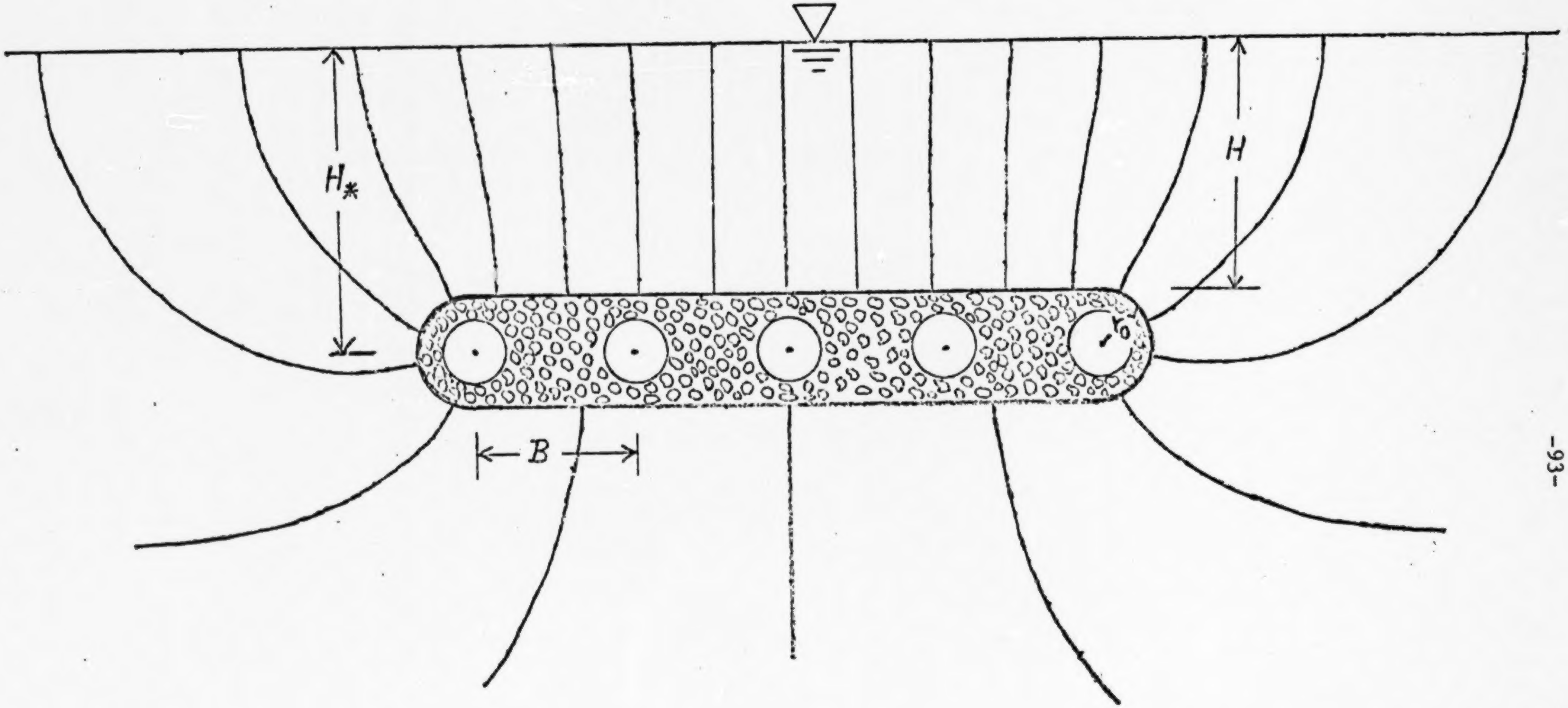

FIG. B-9 - STREAMLINE PATTERN FOR A FINITE LENGTH ROW OF POROUS PIPES BURIED BENEATH THE GROUND SURFACE

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NOTATION

B = center to center spacing of porous pipes;
g = acceleration of gravity;
H = thickness of soil bed above porous pipes;
H_* = vertical distance from the pipe centerline to the earth surface;
K_0 = physical or intrinsic coefficient of permeability;
L = length of pipes;
$\dot{M}$ = three-dimensional mass flow rate;
$\dot{m}$ = two-dimensional mass flow rate;
P = absolute pressure;
P_0 = absolute pipe pressure;
P_1 = absolute atmospheric pressure;
R = universal gas constant;
r_0 = outer radius of circular gravel bed;
T = absolute temperature in degrees Kelvin;
t = time;
t_1 = minimum time required for an element of gas to reach the earth surface;
u = horizontal velocity component;
v = vertical velocity component;
w = complex velocity potential;
x = horizontal cartesian coordinate; real part of z;
y = vertical cartesian coordinate; imaginary part of z;
z = complex variable;
γ = gas weight per unit volume;
ζ = complex variable;
η = imaginary part of ζ; dummy variable of integration;
μ = coefficient of dynamic viscosity;
ξ = real part of ζ; dummy variable of integration;
σ = soil porosity;
ϕ = potential function, real part of w; and
ψ = stream function, imaginary part of w.

APPENDIX C: ANALYTICAL METHODS FOR CHEMICAL ASPECTS OF SOIL FILTER ACTIVITY

Apparatus Used

Gas-Soil Uptake of Hydrogen Sulfide

Five-hundred milliliter erlenmeyer flasks stoppered with black rubber stoppers were utilized for gas-soil uptake tests. Each stopper had a one and one-half inch piece of glass tubing through it. Serum caps were used to cover the glass tubing.

Liquid-Soil Uptake of Sulfide

Standard three-hundred milliliter BOD incubation bottles with glass stoppered tops were utilized for liquid-soil uptake tests. A magnetic stirrer was used to keep the soil in continual motion during the uptake period.

Vacuum Pump

A Precision model 75 vacuum pump capable of delivering a vacuum of 0.1 micron or better was utilized for evacuation of dessicators used in surface area determinations.

Centrifuge

An International centrifuge, size 1, type B, was used to separate the soil from the liquid phase cation solution during the cation saturation treatment of the soil.

Dynamic Uptake Test Columns

Columns to contain the soil were constructed from clear plastic tubing, two and one-quarter inches inside diameter and eight and one-half inches tall. Gas movement was from bottom to top. The lower two inches were filled with Raschig rings to facilitate gas distribution across the entire column cross section. A thin layer of glass wool was placed between the rings and the soil to prevent settlement of the soil into the lower ring packed portion of the column. Rubber stoppers fitted with a glass "tee" were used to cover each end of the column, influent and effluent samples were taken from the base of the "tee".

Experimental Techniques

Gas-Solid Uptake Tests

A modification of the methylene blue method suggested by Jacobs (1957, 1960) was adapted for the testing of gaseous hydrogen sulfide samples. This modification was necessary due to the high concentration of the samples tested. The modification entailed an increase of the color developing reagents, the ferric chloride solution and the N,N-dimethyl-p-phenylenediamine-sulfuric acid solution, to the concentration where they were slightly in excess of the amount required for maximum color development. Extreme care had to be exercised to maintain the sulfuric acid solution only slightly in excess, or results tended to be erratic.

To determine the equilibrium concentration in the erlenmeyer flasks, a three milliliter gas sample was withdrawn from the flasks and injected into a stoppered twenty milliliter test tube, containing ten milliliters of cadmium hydroxide adsorption solution. Precipitation of the hydrogen sulfide in this sample was achieved by several seconds of rapid hand shaking of the test tube. Color developing reagents were then added to the absorption solution container, followed by dilution to 25 milliliters. This diluted sample was analyzed at a wavelength of 760 mμ using a Beckman model DU spectrophotometer. A standard curve was used to convert the absorbance reading obtained spectrophotometrically to concentration of hydrogen sulfide.

Liquid-Solid Uptake Tests

In running the liquid-solid uptake tests, one gram of soil and a varying amount of sodium sulfide solution were mixed with the exact amount of a de-oxygenated buffer mixture to completely fill the glass stoppered bottle. By this method, no gas phase was allowed to be present during the test. The bottles were placed upon magnetic mixers in constant temperature rooms, and stirred until attainment of equilibrium. Composition of the buffer mixtures used may be found in Appendix C.

The concentration of total sulfide remaining at equilibrium was determined by a modified titrimetric method. Twenty-five milliliter samples were withdrawn from the stoppered bottles and added to a mixture of five milliliters of concentrated hydrochloric acid and five milliliters of 0.025 N iodine solution. The iodine remaining after oxidation of the added hydrogen sulfide was back titrated with 0.025 N sodium thiosulfate solution, using starch indicator. The calculations for concentration were performed as suggested by Standard Methods (1960).

The apparatus and technique for uptake studies on the disodium salt of ethylenediaminetetraacetic acid (abbreviated EDTA) were identical to that for sulfide uptake, with the exception that EDTA was substituted for sodium sulfide. A modification of the normal EDTA titration method for water hardness was used for EDTA determination at equilibrium. In this modified method, the titrant used was the equilibrium EDTA-buffer mixture taken from the glass stoppered bottle, while the sample being titrated was prepared from a standard sodium solution and an ammonium buffer solution. Calculations were performed as follows:

$$\frac{\text{mg. EDTA Uptake}}{\text{wt. of soil used}} = \frac{(\text{ml Ca std. used}) \quad \dfrac{\text{mg equivalent of EDTA}}{\text{ml std. Ca solution}}}{\begin{array}{l}\text{ml titrated from}\\ \text{bottle containing}\\ \text{soil}\end{array} \quad \begin{array}{l}\text{ml titrated}\\ \text{from blank}\\ \\ \end{array}} \times 300 \text{ ml.}$$

where three-hundred was the volume of the glass stoppered bottles in milliliters, and the blank was prepared in identical fashion to the other bottles, with the exception that it contained no soil.

Surface Area Determination

A modification of the ethylene glycol monoethyl ether (EGME) method was used to determine soil surface area. The recommended procedure called for replacement of all "fixed" cations in the soil with calcium, because it was felt that such fixation with calcium would create more uniform and reproducible results. However, others have found that when determining soil surface area using ethylene glycol, the saturating cation used determined to a great extent the amount of ethylene glycol retained. In this research, it was felt that altering the cation status in any way was likely to give surface area measurements different from the surface area actually contacted by the hydrogen sulfide. Therefore, no calcium washing was used when determining soil surface areas. Phosphorous pentoxide was used as the dessicant at all times, except for the first evacuation after the addition of EGME, at which time calcium chloride was used.

Soil Sulfur and Sulfate Testing

In the determination of elemental sulfur, the acetone extraction method recommended by Simon and Schollenberger (1925) was used. A turbidimetric determination was selected for sulfate. (Jackson, 1964)

Soil Preparation

Sterilized soils were obtained by placing the soil in a 103°C oven for four days. After this time, no viable organisms could be isolated from the soil on nutrient agar or medias specific for heterotrophic or Thiobacillus bacteria.

Cation saturation was achieved by washing the soil twice with a 10% solution of the chloride salt of the cation desired to saturate the soil exchange sites. Next, quadruple washings with distilled water removed all "free" cations remaining in the saturated soil. All washings took place in plastic centrifuge tubes to alleviate any error due to transfers between the centrifuge tubes and other equipment.

Physical characteristics of Lynden loam were obtained using ASTM recommended testing procedures (ASTM Committee D-18, 1958).

Dynamic Soil Testing

Both wet and dry sterile soils were used in the dynamic uptake testing. Wet soils were prepared from the dry state by spraying water from an atomizer onto a soil sample which was continually mixed. No attempts were made to introduce additional water to the soil once testing began, due to the short term nature of the tests. Although it was realized that more accurate results would have been attained by keeping the soil at a constant equilibrium moisture content through continual water addition, the results attained appear to sufficiently demonstrate the influence of moisture upon hydrogen sulfide removal in a dynamic system.

In the tests requiring soil rejuvenation, the soil was removed from the column and spread out overnight on a newspaper at room temperature to allow contact with air. In all dynamic testing, influent and effluent samples were taken immediately as the gas stream entered and emerged from the soil column. Breakthrough time was selected as the time when the effluent concentration reached 5% of the influent concentration.